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A thesis entitled

The synthesis and properties of some chelating ion exchangers

presented by

HARRY ECCLES

in part fulfilment of the requirements

for the degree of

MASTER OF PHILOSOPHY

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H. Eccles

SYNOPSIS

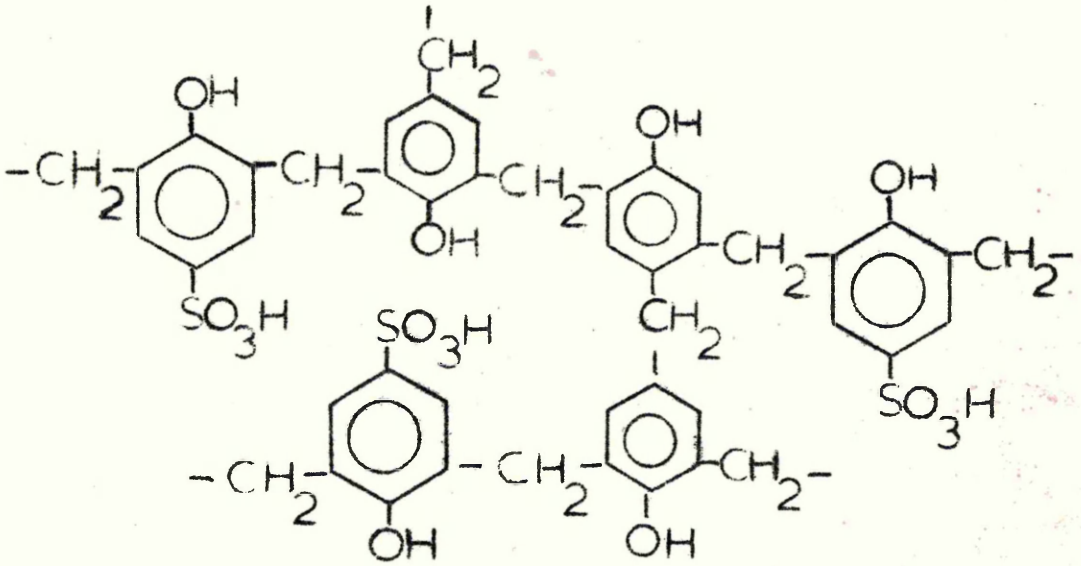
A series of oxine containing polymers, prepared by condensation techniques and by the coupling of oxine to diazotised poly (amino-styrenes), have been investigated in terms of their total capacities for Co(II), Ni(II), Cu(II), Zn(II), Al(III), and UO_2(II) as a function of pH and their rates of equilibration with solutions of metal ions. Other chelating polymers containing salicylic acid, alizarin or pyridyl azo resorcinol as the functional group have also been examined to determine their behaviour with the same six metals.

An attempt to determine the magnitude of the stability constants for the metal-resin complexes, uranyl and copper-polystyrene chelates, has been made. It has been shown that the uranyl values lie somehwat lower than the stability constants of the corresponding metal-monomer complexes, whilst the copper values are of the same order as the corresponding metal-monomer complex.

CONTENTS

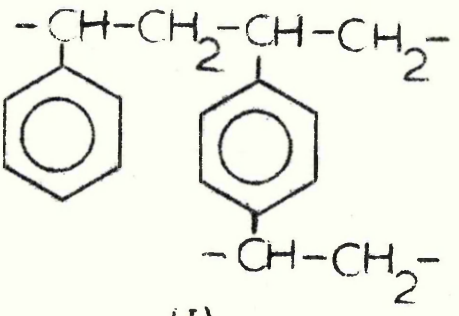
INTRODUCTION

Ion exchange phenomenon was simultaneously discovered by Thompson[1] and Way[2] in 1850 while working with soils containing natural zeolites. This was followed by a period of rapid development of organic ion exchangers. They were first introduced as practical exchangers by Adams and Holmes[3], with the polymeric condensation of formaldehyde with suitable phenols or arylamines. A resin of this nature was prepared by Kressman and Kitchener[4] which involved the reaction of formaldehyde with phenol and sodium phenolsulphonate. The polymeric chains are highly crosslinked through attachment of more than two methylene bridges to the same aromatic ring, of the form:



Kressman and Kitchener's resin had a value of 350 for the total number of exchangeable hydrogen ions, belowpH8. The monomeric weight of the resin was found to be 1714, and from the probable structure it was calculated that 97.5% of the sulphonate

groups were free for ion exchange. Better resins were later introduced by D'Alelio[5], based on the copolymerization of styrene with the crosslinking agent divinyl benzene (D.V.B.) The resulting crosslinked polystyrene, usually prepared in bead form by suspension polymerization, can be sulphonated[5] to produce a cation exchanger, or chloromethylated and treated with a tertiary amine, to produce an anion exchanger[6]. These exchangers have been produced commercially for some twenty years, and have reached high reproducibility of properties, besides being stable and of fairly high capacity. The skeleton of the resin is a copolymer of styrene and p-divinyl benzene, the crosslinked polymer (1) is insoluble, hydrophobic and does not swell with water. The sulphonate cation exchanger (2) is prepared by sulphonation of the beads, the reaction can be performed with concentrated sulphuric acid or with chlorosulphonic acid at 100°C in the presence of a suitable catalyst.



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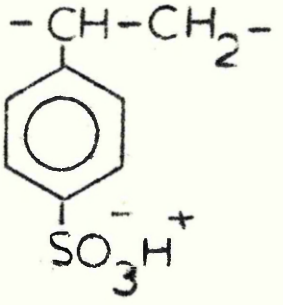
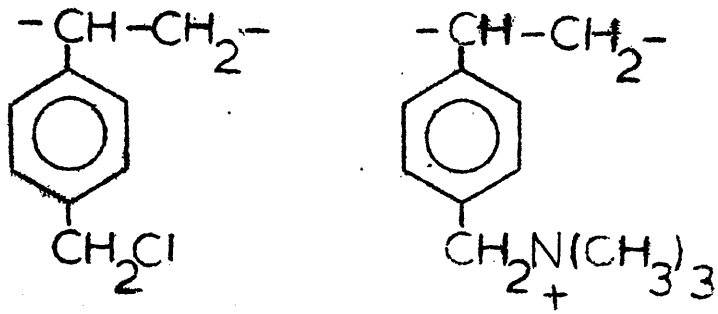


(2)

An ordinary cation resin has a capacity of 5.30 milliequivalents of replaceable hydrogen ions/grm of resin. This figure depends on the degree of crosslinking i.e. the proportion of divinyl benzene used during the preparation.

The quaternary ammonium anion exchanger is prepared by chloromethylation of the polystyrene - D.V.B. beads with chloromethyl ether, using for example stannic chloride as catalyst. The

intermediate (3) is then reacted with trimethylamine to produce the exchanger (4)



(3)

(4)

Early commercial resins showed considerable variation among individual batches, and even among beads within a batch[7,8], that led to differing capacities and swelling and hence selectivities[9]. In recent years however the manufacturers have succeeded in producing adequately homogeneous material. Most of the metal ion separations carried out by ion-exchange chromatography have been based on the stability of their complexes (when a competing chelate is added) or on the differences in the degree of dissociation of the substances being separated. This is best exemplified, in the separation of the rare earths, use is made of their complexes with citric acid or ethylene diamine tetra-acetic acid. This lack of selectivity has not deterred the use of conventional ion-exchangers, in fact using the optimum conditions (i.e. pH and/or complexing agents) and by appropriate selection of eluting agents they can be used for a wide variety of analytical applications. It is the necessary "buffering" of a solution containing metal ions with similar properties, that has restricted ion-exchangers to mostly analytical techniques and water desalination processes.

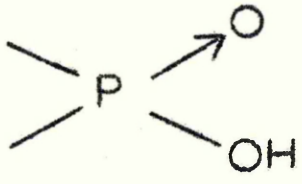
The historical development of analytical methods involving chelates commenced approximately a century ago, with the work of Werner[10]. The present day use and the number of chelates, is too vast a topic to consider here, but one chelate in particular 8 - hydroxyquinoline will be discussed. The discovery of 8 - hydroxyquinoline (oxine) and a few coloured metal complexes was by Skraup in 1883, and during the early twentieth century oxine was used as a precipitant for different metal ions. It was not until 1943 that the extractability of metal oxinates into organic solvents was attempted by Moeller[11]. The procedures used by this author, i.e. 0.01 M reagent solution and four extractions, gave very narrow pH ranges for complete extraction for some metal ions. Other workers [12, 13, 14] have used a 1 per cent reagent solution and have completely extracted metal ions in one operation. Gentry and Sherrington[15] established the pH range for complete extraction of several metals, and found that cupric ions in the presence of tartrate were completely extracted in the pH range, 2.8 to 14. Ferric ions under the same conditions had a similar pH range, but nickel extracted in the range 4.5 to 9.5. Unfortunately, 8 - hydroxyquinoline is a reagent that will form complexes with the majority of metal ions. Phillips[16] in his review article mentions numerous oxinates with particular reference to their stability and structure.

The stability of metal oxinates was investigated by Stary[17] using an extraction technique. The author studied 32 metal oxinates in the presence of competing complexing agents such as oxalic acid, nitrilotriacetic acid and ethylene diamine tetra acetic acid, over a range of pH's. Knowing the stability constant of the metal

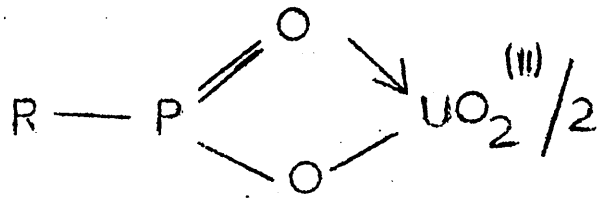
oxinates and dissociation constants for the various complexes used, Stary was able to determine the metal chelate (competing) stability. From his results Stary indicated that ferric ions could be selectively extracted from aluminium (III) at pH 2, the aluminium oxinate extracts above pH 3.0. He also showed that metal oxinates with a higher Ko value (where Ko was the equilibrium constant or extraction constant) could be selectively separated from all other metal oxinates with lower Ko values. It was possibly the knowledge of preferential selectivity of some metal chelates to others that initiated the preparation of resins containing special functional groups. These resins have been designated chelating resins or chelating ion-exchange resins.

The precise origin of chelates used as a means of separating metal ions, using chromatographic techniques was by Erlenmeyer and Dahn[18]. These workers used a column of powdered 8 hydroxy-quinoline and attempted the separation of various cations. During the infancy of chelate ion exchangers only two outlooks were proposed for the choice of chelate. Skogseid[19] and other workers attempted to prepare resins containing groups which were analogous to highly selective organic chelates for example dipicrylamine, O-hydroxy azo compounds and α diketone oximes, in the belief that the polymers will show a high selectivity similar to the monomers. This belief, however, is not true for all resins, for instance Heller and co-workers[20] studying poly-(1-hydroxy-4-vinylpyridinium) resin suggested on the basis of the monomer the N-oxide, that the resin should yield stable co-ordination compounds with uranium or transition metals. The work proved contrary and it was concluded that it may be due to the impossibility of forming suitably directed covalent bonds with two adjacent planar aromatic

N-hydroxy or N-oxide groups. The other concept of choice of chelating agent was advocated by Mellor[21] and later Gregor[22] and Hale [23]. They formulated the preparation of resins containing groups which are notable for the variety of ions with which they complex (oxine or salicylic acid for example). The selectivity of these reagents is obtained by modifying the reaction conditions (cf Stary's work). Several workers have however discounted the likelihood of preparing a completely specific resin. The criterion appears to lie in choosing a chelate which forms complexes of a much higher order of stability with one or two ions than with others. This appears to be the basis of Kennedy and Davies'[24] work, who observed that Th(IV), Fe(III) and UO_2(II) formed relatively strong complexes with organic phosphates and phosphonates containing the group.



Resins containing this type of grouping showed similar behaviour to the parent molecule but with markedly increased stability constants. This was attributed to a combination of the polymer entropy effect and reduced dielectric constant in the resin phase. A chelate resin which the authors prepared was a half-hydrolysed diallyl allyl phosphonate which absorbed UO_2(II) from nitrate solutions at acid strengths of 0.1 to 0.2 N-HNO_3 in the presence of Ca(II), Cu(II) and Co(II). They postulated a 1:2 chelate of the form



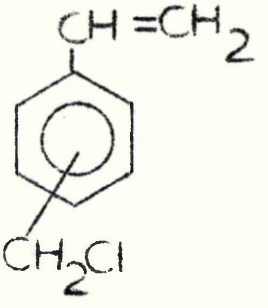
in which the uranyl ion is bound by covalent or partially covalent linkages to the phosphonate functional unit in the resin matrix. The idea that chelate ion exchangers can form 1:2 metal complexes is open to discussion. Where monomers are polymerized, the resulting polymer could form 1:2 chelates, since it may have a high ratio of chelater sites. A resin capable of forming 1:1 complexes is Dowex A-1, an iminodi-acetic acid (IDAA) polymer. Loewenschuss and Schmuckler[25] studied the structure of the resin when containing copper. The resin studied by these workers contained 2.5m mole of iminodiacetic acid/g. of resin and had a capacity for Cu^{2+}, Pb^{2+}, Fe^{3+} and Th^{4+} ions of 2.4 to 2.5 m moles of metal ions/g of Dowex A-1. Because 1g of resin contained 2.5m moles of IDAA it was found that metal ions were complexed by the resin in the stoichiometric ratio of 1:1, independent of valency. This is totally different to the behaviour of IDAA in solution, where metal ions combine with more than 1 molecule of IDAA, in accordance with their valency. The net result of this, is that the complexes in the resin were more stable than those formed in solution.

The synthesis of chelate ion exchangers is historically parallel to that of normal conventional ion exchangers. The preparation of both phenol-formaldehyde condensation polymers and derivatives of polystyrene were used. However, it was a polystyrene resin containing an active group similar in structure to dipicrylamine that was the first chelate ion exchanger prepared.

The resin was synthesized by Skogseid[26] who nitrated polystyrene, subsequent reduction to the amine and reacted with picryl chloride. The synthetic methods used for the preparation of chelate ion exchangers may be divided into various classes.

(1) Polymerization of vinyl-type chelate-forming compounds

The desired polymer is prepared by polymerization of the appropriate monomer. The chelating group may form part of the polymer back-bone or may be attached on the back-bone of the polymer. Chelate polymers of the first type exhibit effects due to the constraints of being part of the backbone. Unfortunately, it is rather difficult to synthesize chelating compounds with vinyl groups attached. Only a few polymerizable chelating compounds have been found, notably (ar-vinylphenylimino) diacetic acid prepared by Morris and co-workers[27]. The starting product was vinyl benzyl chloride (1) a mixture of 80% para and 20% ortho isomers



(1)

A series of vinyl substituted amino acids were prepared as intermediates in the synthesis of chelate polymers. Polymerization of the amino acid monomers, producing homopolymers, was carried out using various catalysts and reaction conditions. Copolymers with vinyl acetate, acrylamide, sodium acrylate and sodium p-styrene sulphonate were also prepared. A number of unsaturated 1, 3 diketones have been prepared. Teyssie and Smets[28] synthesised a polymerizable β diketone, methacroylacetone, by the usual acylation

of an ester by a ketone in the presence of sodium methoxide. The reaction with acrylic and methacrylic ester yielded secondary products in important amounts. A reaction mechanism was proposed for formation of these secondary products which proceeded through an intermediate Michael addition. The preparation of methacrylacetone was also reported by Despic and Kosanovic[29]. These workers investigated the affinity of the copolymers produced from methacrylacetone and ethylene glycol dimethacrylate to ferric and uranyl ions, below pH 7.0. Other workers[30,31] have investigated the structure and stability of polymeric chelates particularly polymethacroylacetone chelates. G. K. Hoeschele and co-workers[32] studied the acid dissociation constant and binding constants for metallic ions in 4/1 dioxanwater solutions for polyvinyl acetonyl ketone and its monomeric analogue acetyl acetone. A modified Bjerrum technique was used to calculate chelation constants, and it was derived that the polymer was equivalent to its monomeric analogue for Cu(II) and three orders of magnitude stronger than its analogue with UO_2(II). A paper published by Degeiso[33] et al. described the preparation and characterization of methacrylylacetyl acetone and its derivatives, and various polymers and copolymers of methacrylylacetyl acetone. Unfortunately, no chelation properties were discussed, but these authors have extensively studied other chelate ion exchangers as will be discussed in later sections. They did prepare derivatives of dimethylglyoxime[34] in particular, monomethacrylyl dimethyglyoxime, also the dimethacrylyl dimethylglyoxime and a homopolymer of the latter. The mono derivative was not easily polymerized with conventional monomers such as styrene and methyl methacrylate. In general the synthesis of polymerizable substances is difficult, especially with large scale techniques. This approach yields

resins of defined structure, but is also hindered by the production of secondary products observed by Smets et al.[28]. The majority of the polymers synthesised in the above manner were soluble in some organic solvents, this is beneficial for detailed studies of the physicochemical behaviour, but is also detrimental for some applications.

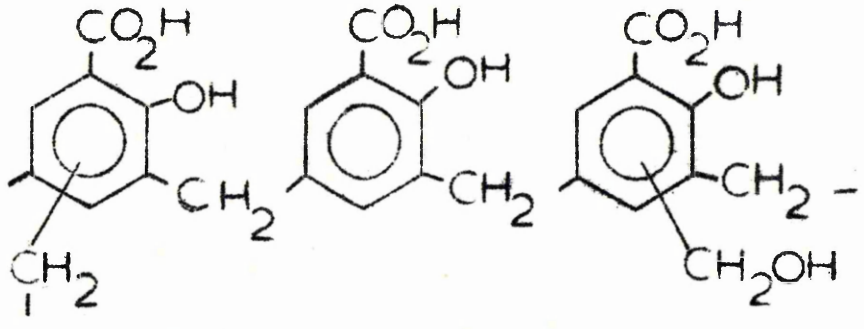
(2) Condensation Resins

In numerous cases the chelating agents, because of their structure are able to enter into condensation reactions as one of the reactants. Aromatic amines, phenol and phenol derivatives are capable of this. In general formaldehyde (or other suitable aldehydes) and a crosslinking agent, together with the chelate condense to form a resin gel. Several papers have been published concerning condensation chelate ion exchangers, although Millar[35] has strongly criticised the technique. The difficulties lie in insufficient control of crosslinking, none too stable products and the conditions employed may destroy or alter the chelating sites present in the monomer. Several papers describing the condensation of phenol (or its derivatives), formaldehyde (and/or furfuraldehyde) and 8-hydroxyquinoline have appeared over the last twenty years. Lillin[36] prepared such a polymer, but the information concerning it was very brief. Parrish[37] prepared a resin from oxine, resorcinol and formaldehyde which showed some chelating properties similar to those of oxine itself, but the capacity of the resin was very low. This is in complete contrast to the resin prepared by Pennington and Williams[38], their resin had a capacity for Cu(II) at pH7 of approximately 4.0m moles/g. of resin. This resin had the greatest selectivity of all their resins tested, and its capacity

was equal to that of Amberlite IRC-50 (carboxylic acid ion-exchange resin). These condensation oxine resins were prepared in strong alkaline conditions, Degeiso[39] and co-workers prepared both acid and base catalysed oxine-formaldehyde polymers. The acid catalysed polymers had the advantage of lower molecular weights and were soluble in some organic solvents. They attempted to show the degree of crosslinking with capacity for metal ions, by preparing various resorcinol cross-linked polymers incorporating oxine. Unfortunately, only one set of results were given for the crosslinked polymers and showed a significant decrease in capacity, compared with the linear 8-hydroxyquinoline - formaldehyde polymer. The rate of equilibration of these resins was not attempted, but they did prepare a series of crosslinked (using resorcinol), 8-hydroxyquinoline-formaldehyde, base catalysed polymers. These resins were not investigated, a few properties referring to solubilities were however quoted. A recent technique used for preparing oxine condensation polymers was published by Bernhard and Grass[40]. They obtained the resin by direct condensation of metal oxinates with resorcinol and furfuraldehyde, whereby the arrangement of the planar 8-hydroxy-quinoline groups became independent of the preparation. A separation of Ru, Zr, U and Ce was accomplished by using the polymer derived from Ba-oxinate. A polymer derived from Na-oxinate was used to separate Sr^{90} and Y^{90}. In a later paper[41], they showed by means of the distribution coefficients, that the selectivity of chelate resins depended on the addition of certain ions e.g. Ba and Al during the preparation.

Copolymerisation of salicylic acid with phenol and formaldehyde under acidic conditions at 100°C has been carried out by Japanese workers[42,43,44], but the capacities appear to be

rather low. The method of their determination did not differentiate between carboxylic and phenolic functionality. As there was some evidence for decarboxylation of salicylic acid under strongly acidic conditions at 100°C, Davies[45] et al condensed salicylic acid under slightly alkaline conditions with formaldehyde and using resorcinol as copolymer. Resorcinol was used in place of phenol of the Japanese workers since the phenol copolymer was found to leach considerably on acid-alkali recycling. The sodium and copper capacities for the salicylic acid-formaldehyde resorcinol copolymer were 2.4m equiv/g of resin in the hydrogen form (at the first equivalence point) and 3.2m equiv/g respectively. Using slightly acidic conditions, Degeiso and his co-workers[46] condensed salicylic acid with formaldehyde producing a water-insoluble polymer which had an average molecular weight of 6700± 15%. The analyses and neutral equivalents compared favourably with the structure (1).



(1)

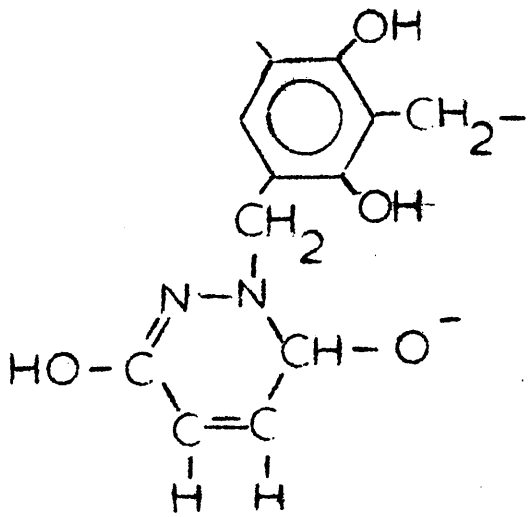
The polymer was soluble in several organic solvents and in aqueous bicarbonate, carbonate and alkali solutions. This polymer was extensively studied by the authors, five metal-ion complexes were prepared and identified using infra-red spectra, thermal decomposition measurements and elemental analysis.

In a later paper[47], these authors using the same resin determined rates of equilibration and capacities for several ions. They concluded that the resin was selective for uranyl ions over all other metal ions they investigated. They verified this statement, by removing uranium from uranium ores using this resin and compared the salicylic resin with a resorcylic acid-formaldehyde resorcinol copolymer[48]. From the results they obtained they concluded that the salicylic acid polymer was a stronger acid than the resorcylic acid polymer, and therefore uranyl ion bound to the former should be more stable at pH2. The purity of the uranium eluted from these resin was generally $> 90\%$.

A number of condensation polymers formed from m-phenylenediglycine and formaldehyde, or anthranilic acid, resorcinol, o-aminophenol and formaldehyde[37,38,49] have been prepared. Such polymers form complexes with Mg(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) at pH5. The o-aminophenol resin prepared by Gregor and co-workers[49] had a capacity for Fe(II), Co(II) and Ni(II) of 0.20 to 0.40 m moles/g of resin. Gregor attributes this equivalent absorption to complex formation between the amine groups of the resin and metallic cations. A similar synthesis was adopted by Pennington and Williams[38] for the preparation of o-aminophenol resin. However, their resin had a capacity of 2.5 m moles of Cu(II)/1 g of resin at pH 5.0. The difference could be due to Gregor using 0.001M metal ion solutions and Pennington and Williams 0.01M metal ion solutions for capacity measurements. This appears unlikely however, since an increase in 10 fold concentration of metal ion, results in a five fold increase in capacity. This is certainly applicable to copper and Gregors' m-phenylene diglycine resin. A reasonable explanation was provided by Parrish, who suggested that the resin made by Gregor

et al. from o-aminophenol and formaldehyde would be expected to contain substituted amino groups. To overcome this difficulty Parrish synthesised an o-aminophenol resin starting from o-nitrophenol, resorcinol and formaldehyde, and then reducing the nitro group. This resin exhibited chelation properties, and it was possible to separate copper from calcium on a 10-cm column of the resin at pH 5.5. Pollard, Nickless and Cooke[50] also synthesised such resins containing o-aminophenol, m-phenylene diglycine, anthranilic acid and resorcinol. They used them to separate such metals as magnesium and copper.

Condensation of cyclic maleic hydrazide with formaldehyde in the presence of resorcinol leads to an ion-exchanger (1). This resin [51] was reported to be specific for Hg(II) and mercurous ions in weak acid solutions



(I)

Chelate ion exchangers formed by condensation of formaldehyde and its derivatives, with various crosslinking agents and the appropriate complexing agent have certain disadvantages. In general such resins have slow rates of metal ion uptake, due to the high density of the polymers. Millar[35] exemplifies his criticism by referring to

the preparation of pyrogallol carboxylic acid resins of Parrish[37] and the β-resorcylic acid resins of the Chemical Research Laboratory, Teddington[52]. He suggests that much of the carboxylic function may have been lost during condensation, in which the carboxyl group, labilized by ortho- and para-hydroxyls is replaced by an entering methylene group. Pollard, Nickless and Cooke[50] also had difficulty in preparing consistent polymers containing β-resorcylic acid and its derivatives. Deuel and Hutschneker[53] suggested that in condensation resins, the chelating agent would not be chemically bound to the polymer network, but possibly held by molecular entanglement.

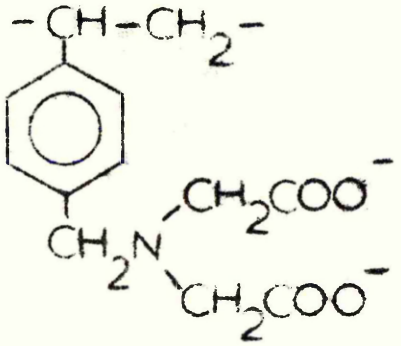
3. Subsequent Introduction of chelating groups into condensation resins

In a few cases it is possible to synthesize the resin maxtrix by condensation and then to introduce the desired chelate molecule by subsequent reaction with the solid matrix. A typical example of this process is o-phenylene bis (oxyacetic acid) resin[54,55,56]. In the first step (o-hydroxyphenoxy) acetic acid, pyrocatechol and formaldehyde are condensed, forming an insoluble resin. In the second step the free phenolic groups are converted to ether groups by reaction with chloroacetic acid. This resin[53] was reported to be specific for zirconium. The influence of the conditions of the preparation on the quality of the resin, expecially the rate of crosslinking was investigated. The capacity of the most favourable product was 2.1m moles of Zr/g of resin at pH 4.7. A resin which complexed copper at low pH was prepared by Parrish[37], who diazotized a resin of the o-aminophenol type and coupled it

with 2-naphthol. This resin contained the OO'-dihydroxy-azo grouping which is present in certain metallized dyes. This method of preparation is only slightly better than condensation techniques, the resins usually have slow rates of metal ion uptake.

4. Reactions on solid vinyl polymers

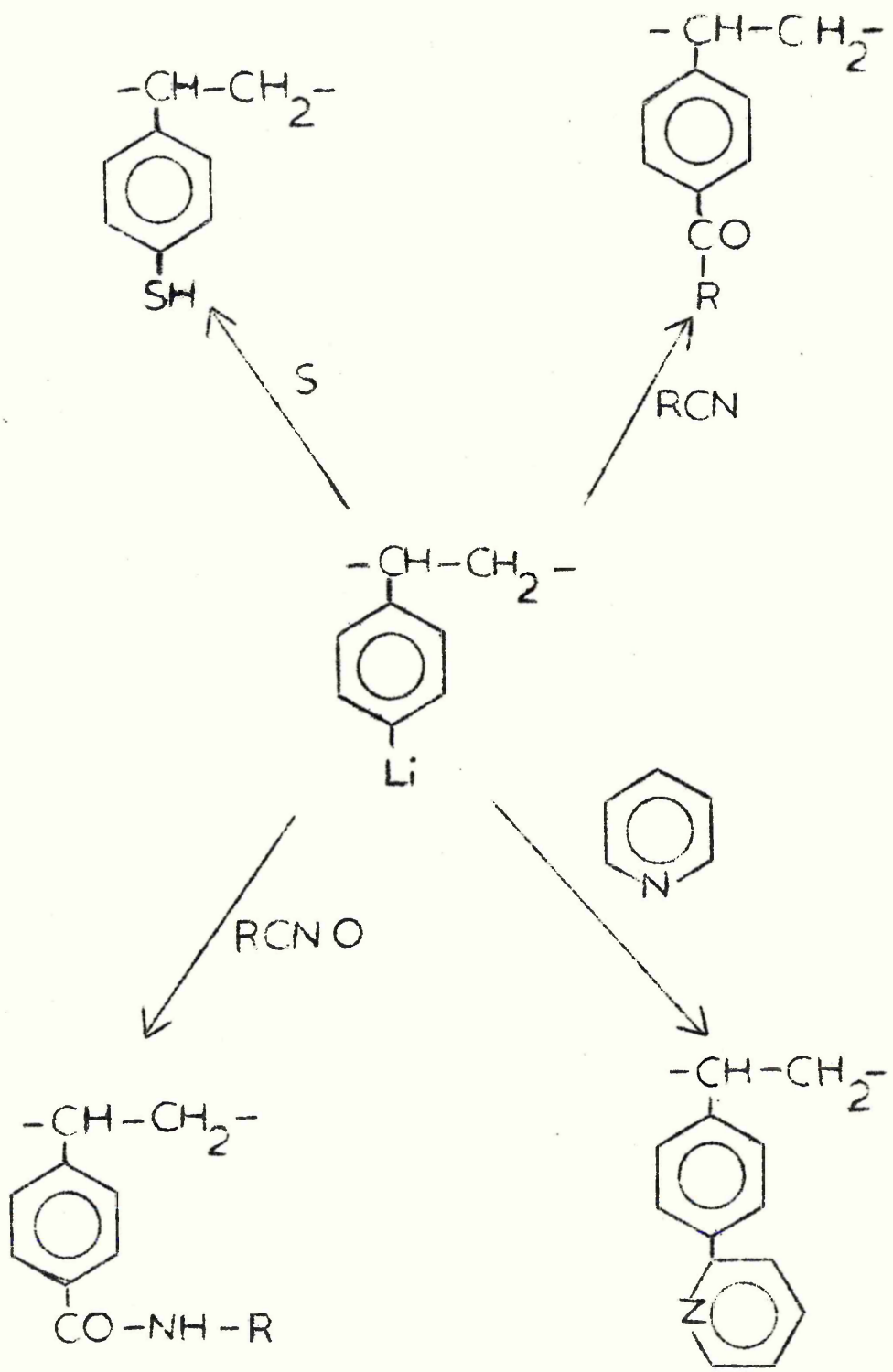
Solid styrene polymers used as starting materials for the synthesis of chelate ion exchangers offer several advantages. The polymers are inexpensive and of uniform composition, and the spherical shape of the beads provides mechanical strength and ease of operation. It has been shown however that most of the well known organic reactions when performed on high polymers, take a disadvantageous course owing to intramolecular reactions within the resin gel [57-61]. Moreover, each subsequent reaction will progressively clog the pores of the polymer, the yield of the desired functional groups is often less than 20% (based on the starting material)[62]. The most favourable results have been obtained with chloromethylated polystyrene. This has been used in the preparation of Dowex A-1, manufactured by the Dow Chemical Company.



The preparation, properties and analytical applications of this resin have been reported in numerous papers. Ideally reference should be made to Dow's manual describing chromatographic separations[63].

A technique used by several workers is nitration of polystyrene, reduction to the amine, diazotisation and subsequent coupling with the desired chelate. Parrish[64] used this product and prepared a resin incorporating 8-hydroxyquinoline. The rate of absorption of metal ions was slow, two weeks were required for the attainment of equilibrium. It was found that copper, nickel, and cobalt were strongly absorbed in the pH range 2-3. Zinc, manganese, aluminium, magnesium and calcium were not taken up below the pH values 1.5, 2.0, 2.8, 4.0 and 4.8 respectively. The uptake of copper ions was enhanced by the presence of chloride ions in the pH range 0.5-1.5. This could be attributed to the residual amine groups left on the benzene nucleus (approximately 40% left as coupling was only 60% efficient) behaving as anion exchanger with the $(Cu\ Cl_4)^{2-}$ species. Coupling of 8-hydroxyquinoline to styrene in this manner was also used by Davies[45] et al, unfortunately only the capacity of the resin for copper ions was quoted (1.4m equiv/g H^+ form of resin).

A possible starting material for preparation of polystyrene chelating polymers is poly-p-lithium styrene[65]. This may be prepared from poly-p-iodostyrene[66] with butyllithium, the iodine could be exchanged almost quantitatively with lithium, no inter or intra molecular side reactions being detected[67]. A selection of the reactions which have been carried out are given:-


-CH-CH2-
SH
S
-CH-CH2-
CO
R
RCN
-CH-CH2-
Li
RCNO
N
-CH-CH2-
CO-NH-R
-CH-CH2-
Z

A paper describing the preparation of cross-linked polymers derived from 4-hydroxystyrene was published by Packham[68], and later used by Blasius[69]. Normal electrophilic substitution reactions on poly-4-hydroxystyrene are restricted to the position ortho to the hydroxyl group, and thus lead to polymers with potential chelating functions. The polymers were prepared from 4-acetoxy styrene, D.V.B., and $\alpha\alpha^1$-azo-bisisobutyronitrile in benzene at 65°C. Hydrolysis of cross linked poly-4-acetoxystyrene proceeded smoothly in alkaline aqueous dioxon. Subsequent reactions were carried out, resulting in the formation of approximately twenty polymers, having functional groups ranging from $-SO_3OH$ to $-C(Me)=N-OH$. The highest combined capacity for nickel and copper was for the 3, 5-$(SO_3H)_2$ resin (5.97 m equiv/g), $-C(Me)=N-OH$ (1.18 m equiv/g), whilst a methyl ketone derivative had no affinity at all.

A chelate ion exchanger[51] reported to be specific for copper ions, was prepared when a styrene-divinylbenzene-maleic anhydride copolymer was treated with hydrazine. The hydrazine-treated copolymer was then converted to the oxalyl derivative.

The preparation of chelating polymers using the techniques described in this section appear to be relatively successful. This is indeed so in the case of Dowex A-1, probably the most widely studied polymer. The procedure used by Parrish and Davies et al, namely diazotisation of chelate molecules on to polystyrene is a somewhat precarious scheme. Bazilevskaya[70] and co-workers reported the conditions for azo coupling of polystyrene diazonium chloride with oxine. Azo coupling depends on time, temperature, solvent and pH. Probably the most interesting analogues of polystyrene since the chloromethyl derivative are the poly-p-lithium and the 4-hydroxyl derivatives.

Regardless of synthetic procedure adopted, Gregor[49] suggested that a chelate group suitable for use in a resin must have the following properties:

(1) be capable of resin formation or substitution in a resin matrix;

(2) be sufficiently stable to withstand the polymerization or resinification reaction; and

(3) be compact so as not to be hindered sterically by the dense resin matrix.

An additional requirement is that both arms of the chelate structure be present on the same monomer in proper spatial configuration. In addition to these criteria for the chelate, Blasius and Brozio[71] suggested that the resin itself should have, in addition to the demanded selectivity, sufficient mechanical and chemical stability, especially towards acids and bases. The resin should also have an effective exchange capacity of at least 1m equiv./g of air dried resin, and the rate of the complexation reaction to be relatively high. Chelating ion-exchangers are distinguished from the ordinary type of ion-exchanger by three main properties.

(a) <u>High Selectivity</u> - The affinity for particular metal ions to a certain chelating ion-exchanger depends mainly on the chelating group and not on the size of theion, its charge or other physical properties which affect ordinary ion-exchangers.

(b) <u>Bond Strength</u> - In ordinary ion exchangers the bond strength is of the order 2-3k.cal/mole and exclusively electrostatic, with chelate ion exchangers the bond energy is 15-25k.cal/mole.

(c) <u>Kinetics</u> - With conventional ion-exchangers, the exchange process is more rapid and controlled by diffusion only. The

exchange process in a chelating exchanger is slower and controlled by a particle diffusion mechanism or by a second order chemical reaction.

Although above 150 papers have been published on chelate ion-exchangers, the value of much of it is suspect, either on account of failure to characterize the material adequately, or because of insufficient evidence of chelation. Nickless and Marshall[72] in their review article are strongly critical of such papers, but emphasize that study of chelate formation is not easy even in simple systems. Gregor and co-workers[73] determined the stability constants of metal ions with the resins polyacrylic acid and polymethacrylic acid, by potentiometric titrations of the resin with sodium hydroxide both in the presence and in the absence of complexing metal ions. In order to calculate the constant from experimental data they used a modified Bjerrum's method. Teyssie[30], used a distribution technique to evaluate the binding constants of a dispersed suspension of polymethacroyl acetone for copper and nickel ions. In addition to indicating that the resin had a larger binding constant for copper than nickel, they also suggested that the physical shape of the polymer was important. Using a similar type of distribution technique, Loewenschuss and Schmuckler[25] determined the stability constants of Cu(II) andNi(II) complexes of Dowex A-1. In this method various competing chelates were used whose concentrations were constant, but the quantity of resin used was varied. This method is defined as being "anti-Schubert", since Schubert's[74] method which is well known for the determination of stability constants of complexes, uses conventional ion exchangers (constant amounts) and varies the competing chelate. Both methods result in initially the derivation of the distribution coefficient which is dependent on competing chelate-metal ion stability. Other

papers involving chelate formation of metal ions with Dowex A-1 which are informative have been presented by Schmuckler[75] and Eger and co-workers[76]. There are numerous other publications involving chelating properties and properties in general of both Dowex A-1 and other chelating ion exchangers which have been mentioned in several review articles[23,53,71,72,77-80].

The applications of chelate ion exchangers are few, with the exception of course of Dowex A-1. Three chelating ion-exchangers were evaluated by Davies and co-workers[81] for the extraction of uranium from sea-water. Their performances were compared with conventional ion exchangers and inorganic absorbents e.g. basic zinc carbonate, titanium hydroxide and lead sulphide. In general the authors found the inorganic absorbents to be superior, due to the poor rate of uptake of both ion and chelate exchangers.

Uptake of uranium from sea water

Absorbent	Time of contact (days)	Uptake ug/g of dry H^+ form	Functional group
Zeocarb 226 resin	36	1.5	COO Na
8-hydroxyquinoline resin	81	13	$-N=NC_9H_5NONa$
Resorcinol arsonic acid resin	112	1,010	$-AsO(ONa)_2$
Basic Zinc Carbonate	23	512)	uptake (ug/g
Titanium hydroxide	21	268)	of metal base)

In a recent article by Gaskell[82], the author forecasts the possible use of an economic ion exchanger for the removal of uranium from sea water. A poly-(triaminophenol-glyoxal) chelating polymer[83] was coated on an inert support and used in column chromatography followed by atomic absorption spectrometry to determine copper concentrations.

The Aims of this Investigation are:

(1) An attempt to clarify the situation regarding chelate ion exchangers incorporating 8-hydroxyquinoline as the functional group. Resins will be prepared and evaluated using both condensation techniques described by Pennington and Williams[38] and Degeiso and co-workers[39]. The procedure of azo coupling chelate molecules to a polystyrene - divinylbenzene copolymer will also be attempted.

(2) The synthesis of a molecule containing both chelating and crosslinking properties will be undertaken, since Parrish[37] found it necessary to add resorcinol as the crosslinking agent in the preparation of his o-aminophenol-formaldehyde polymer derived from o-nitrophenol-formaldehyde. Such a molecule is 4-Nitroso-resorcinol, which should undergo condensation to give a polymer in alkaline solution. Phenol may be incorporated in the resinous matrix to observe the effect of the degree of crosslinking on metal ion capacities and kinetics.

(3) Both condensation resins and polystyrene polymers containing the chelate molecule salicylic acid will be prepared. Although literature appears to be favourable for such systems, it has been reported by Rabek[84] et al. that the possibility of chelate formation with salicylic acid is unfavourable.

(4) Resins incorporating 1, 2 dihydroxy anthraquinone (Alizarin) have been prepared previously, but they have only been evaluated as redox polymers[85]. It is possible that such resins have sufficient capacities for metal ions to warrant investigation.

(5) The chelate molecule 4-(2-pyridyl azo) resorcinol (PAR)[86,87], has not been used previously with chelate ion exchangers. It has however been used in conjunction with conventional ion-exchangers as a spot procedure for detecting heavy metals[88]. Resins containing

PAR functional groups should have superior selectivities for Cu(II) over Ni(II), and for UO_2(II) over Zn(II). Since the log k_1 values of the PAR chelate monomer with UO_2(II) and Cu(II) are greater than those of Ni(II) and Zn(II) by a factor of approximately 10^3.

EXPERIMENTAL

(A) Preparation of chelate ion exchangers incorporating 8-hydroxyquinoline molecules

(1) Direct condensation methods

(a) Base catalysed procedure

The procedure adopted was identical with that described by Pennington and Williams[38]. The yellow suspension formed on addition of 8-hydroxyquinoline (oxine) to a solution of sodium hydroxide, reacted gradually with formaldehyde when added, to produce a deep red solution, in which all the oxine used was soluble. The formaldehyde was allowed to react with the oxine for a further 1 hour, after which an alkaline resorcinol solution (containing an equimolar quantity of resorcinol to oxine) was added, followed by a further addition of formaldehyde. The resulting solution was placed on a water bath for 15 minutes, which produced an almost black gel. This gel was cured in an air oven at 110°C for several hours. The almost black resin was ground in a mortar, and screened to give a fraction 30's-60's mesh size. The resin was washed thoroughly with water, 0.1m sodium hydroxide, water, 0.1m hydrochloric acid, and finally with water until nearly neutral. The pH of the final washing was 3.5, which could not be improved by further washing with deionised water (pH 5.2). The resin particles changed colour during this HCl- washing procedure, from red to orange-brown, but continual washing with water restored the original dark red colouration. The resin was air dried and stored in a tightly stoppered bottle. A thoroughly dried sample of the resin was retained for elemental micro analysis.

(b) Acid catalysed procedure

This method was identical with that used by Degeiso et al[39]. The oxine, resorcinol (equimolar ratio to oxine) and aqueous formalde-

hyde solution were heated on a steam bath until a homogenous melt was formed. A small quantity of oxalic acid was added, and the mixture heated until it solidified. A volume of water was added to the orange-red solid and further heating continued for 1 hour. Absorption of the water occurred after 1 hour, and 1 ml. of concentrated hydrochloric acid added. Heating of the organge-red solid occurred for a further 16 hours, after which time the solid was crushed and screened.

The 30- to 60- mesh portions of the resin were washed thoroughly with water, and left Soxhlet extracting with ethanol overnight. This procedure was to remove any unreacted oxine and any low molecular weight polymers. The ethanol extracted resin was washed with 0.1m - HCl and finally washed with deionised water until nearly neutral (pH of final washing was 3.5). No colour changes were observed during washing procedures, the colour of the resin was orange-red. The resin was air-dried, stored in a stoppered bottle, and a dried sample of the resin submitted for elemental microanalysis.

(2) Azo coupling of the chelate molecule to a suitable condensation matrix

(a) Preparation of a p-nitrophenol-formaldehyde phenol copolymer

Sodium hydroxide (0.90 moles) was dissolved in the minimum amount of water, the p-nitrophenol (0.30 moles) was added and constantly stirred. To the yellow suspension formed, phenol (0.30 moles) was added, followed by the careful addition of paraformaldeyde (0.90 moles). During the addition of paraformaldehyde a vigorous reaction ensued. The resulting black gel was cured

in an air oven at 134°C for two days. The brittle mass obtained was crushed in a mortar andscreened, the 30's - 60's mesh size retained.

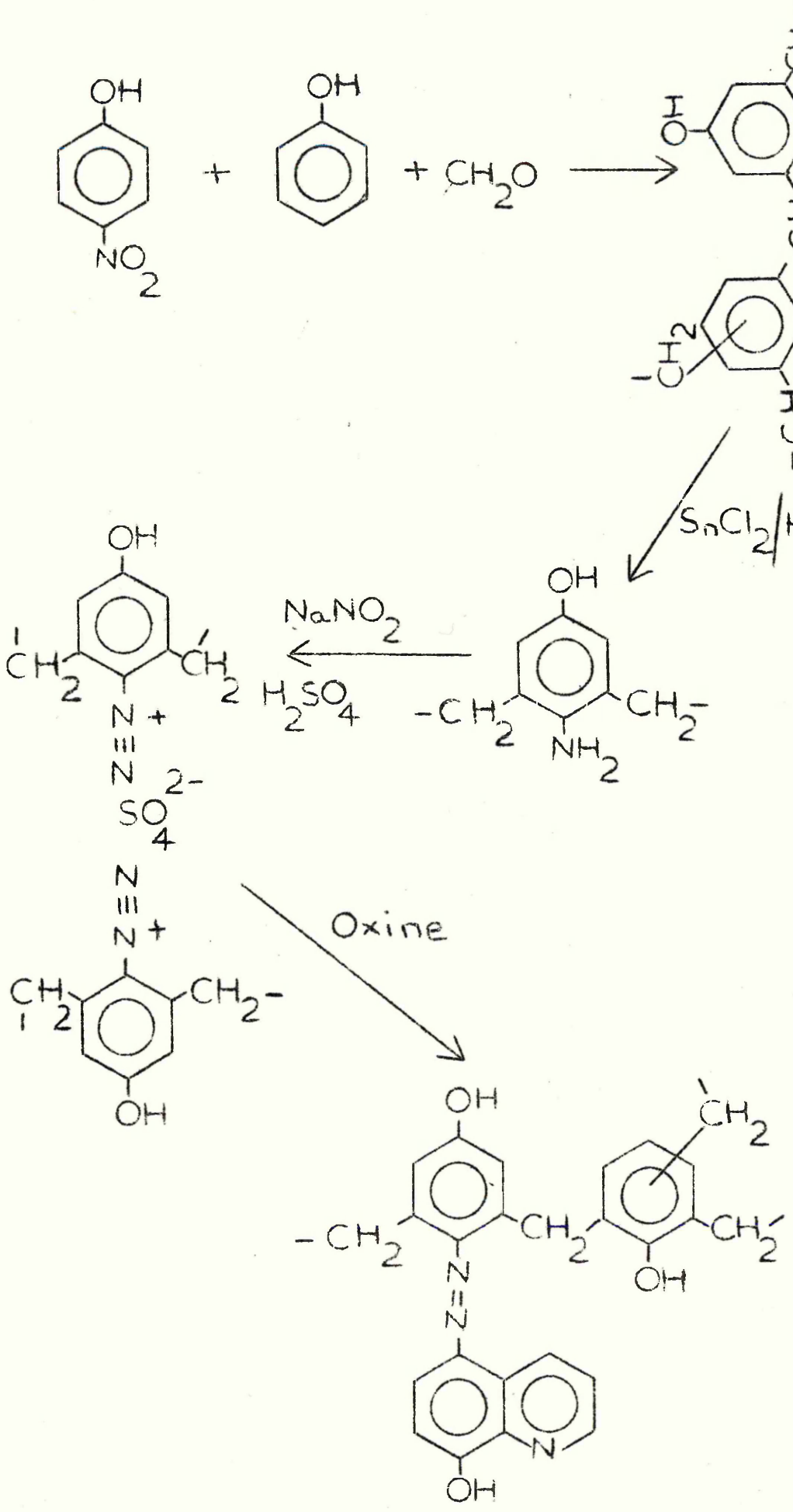
The colour of the resin was dark green, it was allowed to Soxhlet extract using ethanol for 16 hours. A small quantity was retained, which was further washed with 0.1m-HCl, the colour of the resin changing from green to red. Thesample was washed with deionised water, air dried and stored in a stoppered bottle. A small quantity of this was dried and submitted for elemental microanalysis. The bulk of the p-nitro-phenol-formaldehyde phenol copolymer was reduced to the amino derivative. The resin was placed into a 1-litre round bottom three neck flask. The flask was fitted with a mechanical stirrer (with a mercury seal) and a water condenser, whilst the third neck was stoppered. Stannous chloride (1 mole) was dissolved in approximately 500 ml of concentrated hydrochloric acid and 200 ml of water. This solution was poured into the flask, and allowed to react with the resin at 90-100°C for five days with continuous stirring. After reduction had occurred the solution was decanted from the resin, and the solid washed several times with water. The resin was washed several times with 2m sodium hydroxide solution (to destroy the $(R\text{-}NH_3)_2SnCl_6$ complex), water, 0.1m-HCl and finally with deionised water. A small portion was retained, allowed to air dry and stored.

Microanalysis and the determination of amino groups by non-aqueous titration[89] were obtained. The colour of the resin had darkened slightly. Themoist amino resin was converted to the diazonium sulphate. To a well stirred suspension of the resin in approximately 1500 ml of ice-cold water, 375 ml of 1.0m sulphuric acid and 0.5 mole of sodium nitrite (dissolved in 300 ml of water) were added dropwise, simultaneously. The reaction vessel was

externally cooled between 0° and 5°C. After addition of the acid and nitrite solution, the resin was allowed to diazotize for 18 hours with constant stirring and external cooling maintained. The acid/nitrite solution was decanted off, and the diazo polymer washed several times with ice-cold water. The polymer was added to an ice cold solution of 8-hydroxyquinoline (0.30 moles) in aqueous alcoholic (1:1) sodium hydroxide (1.5 moles). The rate of addition of the resin was over a period of 1 hour. Stirring was continued for a further 7 days between 0 and 5°C. The excess solution was decanted off, the resin washed several times with ethanol, and allowed to Soxhlet extract using ethanol for 16 hours. This procedure was mainly to remove any oxine that had precipitated during the coupling procedure. The polymer was washed with water, 0.1M-HCl and finally with deionised water. The sample was allowed to air dry and screened, the portions passing the 30- mesh and retained on the 60- mesh screen were stored in a stoppered bottle. Again a perfectly dry sample was submitted for analysis. The colour of the final product was brown-red.

Reaction sequence

(See over)


OH
NO2
+
OH
+ CH2O
CH2
NO2
OH
CH2
CH2
OH
CH2
CH2
SnCl2/HCl
OH
NaNO2
H2SO4
CH2
CH2
N +
N
2-
SO4
OH
CH2
CH2
NH2
N
N +
CH2
CH2
OH
Oxine
OH
CH2
CH2
CH2
CH2
OH
N
N
OH

(b) Preparation of 4-Nitroso-Resorcinol-formaldehyde polymer and copolymers of the same with phenol

Four resins were prepared, one a 4-Nitroso-Resorcinol-formaldehyde polymer and three copolymers of 4-Nitroso-Resorcinol-formaldehyde with phenol. The 4-Nitroso-Resorcinol was prepared according to Henrich's method[90]. The procedure essentially involves the reaction of isoamyl nitrite with resorcinol in alcoholic potassium hydroxide solution, at 0°C. The resulting red solid was washed with ethanol and finally with ether. The red potassium salt was not converted to the "free" 4-Nitroso-Resorcinol as the latter is much less stable. The potassium salt of 4-Nitroso-Resorcinol (0.20 mole) was dissolved in a small quantity of water containing sodium hydroxide (0.20 mole). To this dark red solution an aqueous solution of formaldehyde (0.40 mole) was added carefully. A vigorous reaction ensued, the temperature of reactants rising to 90-100°C. The dark almost black solution was cured in an air oven for 7 days. After approximately 4 hours during the solution began to "gel". This resin was designated No.1. Three other resins were prepared in a similar manner to the above procedure but varying amounts of phenol were added to each i.e. Resin No.2 contained an equimolar amount of phenol (0.20 mole), Resin No.3 0.06 mole of phenol, and Resin No.4 0.12 mole of phenol. A similar increase in temperature was observed on addition of formaldehyde, but in general the time taken for the solutions to gel was longer than for Resin No.1. Resins 2,3 and 4 were also cured for 7 days at 100°C. All four samples were ground separately in a mortar to 30-60's size. The resins were Soxhlet extracted using ethanol for 16 hours. A small quantity was retained from each, which was

further washed with 0.1M-HCl and finally washed with deoinised water. The bulk of these samples were air dried and stored in bottles, a small quantity of each was thoroughly dried and microanalysis obtained. TheSoxhlet extracted resins were converted to the amino derivative as described previously (2(a)) but using 0.50 mole of stannous chloride, 250 ml of ethanol and 250 ml of concentrated hydrochloric acid. The reaction period was 7 days at a temperature of 70-80°C. The procedure for washing the resin was identical with that described in 2(a). Air dried samples were retained in stoppered bottles and perfectly dried samples submitted for microanalysis and estimation of amino groups. The four amino polymers were converted to the diazonium sulphate derivative using 250 ml of molar sulphuric acid and 0.30 moles of sodium nitrite dissolved in 200 ml of water. The technique used was similar to that described previously. The coupling of the azo polymers to oxine (0.20 moles) in an ethanol-water solution (1:1) containing sodium hydroxide (1.0 mole) was also standard practise. The washing, screening and sampling techniques were exactly the same as in the preparation of the p-nitrophenol-formaldehyde phenol copolymer.

(3) Azo coupling of oxine molecules to a polystyrene-divinylbenzene dopolymer

The starting material was a lightly cross-linked polystyrene-divinylbenzene bead, mesh size 20-30. (Amberlite XAD-2) manufactured by Rohm and Haas, Resinous Product Division. The synthetic procedures employed have been previously used by Davies et al[45] who nitrated swollen beads using a fuming nitric acid/concentrated sulphuric acid mixture at 70°C. The nitroderivative was reduced to the poly(amino styrene) using stannous chloride. The diazonium

compound was prepared via sodium nitrite/hydrochloric acid, and this in turn was coupled to 8-hydroxyquinoline at 0°C to 5°C. Samples of the nitro and amino polystyrenes were retained and thoroughly washed with water, Soxhlet extracted with ethanol for 16 hours, washed with 0.1m-HCl and finally with water. This washing procedure was also used for the polystyrene azo-oxine polymer. Samples of the nitro, amino, and azo oxine polymers were submitted for micro-analyses, but were previously crushed and dried thoroughly. A perfectly dried sample of the amino derivative was analysed for the number of amino groups present.

The nitration and reduction steps were carried out on approximately 150 grms. of polystyrene-divinylbenzene copolymer. Only one-quarter of the poly amino styrene was diazotised and coupled to 8-hydroxyquinoline. The remaining three-quarters was used in azo coupling of other chelates. This procedure was adopted so that the nitro and amino polystyrenes would have the same original percentage composition.

B. Preparation of salicylic acid chelate ion exchangers

(1) Direct condensation technique:

This procedure is similar to Pennington and Williams'[38] i.e. involves base catalysed condensation. Sodium salicylate (0.5 mole) and sodium hydroxide (0.12 mole) were ground together. The mixture was placed in the reaction vessel (normally a suitably sized chemical jar was used and the mouth plugged with cotton wool before curing) and aqueous formaldehyde solution (0.25 mole) added. The mixture was warmed for a week at 40°C, a creamy white product formed. The temperature of the oven was increased to 100°C and the reaction allowed to proceed at this temperature for two days. There was

little change observed in the product, which was easily crushed but soluble in water. The creamy coloured product was thoroughly ground, mixed with resorcinol (0.50 mole), and aqueous formaldehyde solution (0.12 mole) added. This mixture was cured at 100°C in an air oven for one week. The red resin produced was crushed, collecting the 30-60 mesh size.

These fractions were washed with water, and allowed to Soxhlet extract using ethanol for 16 hours. The resulting polymer was washed with 0.1m-HCl and with deionised water. The resin was allowed to air dry and stored in a tightly stoppered bottle.

(2) Azo coupling of the chelate molecule to polystyrene-divinylbenzene matrix:

Coupling of salicylic acid in alkaline solution was achieved as described previously in A(3). Approximately 40 grms of poly-amino styrene were diazotised and allowed to react with salicylic acid (0.30 mole). The washing procedures were as described previously. The final resin was air dried stored in a stoppered bottle, and a thoroughly dried sample submitted for micro analysis.

In addition to obtaining microanalysis of the polystyrene azo-salicylic acid, both salicylate containing resins, were analysed for total number of replaceable hydrogen ions.

C. Preparation of 2, 4 dihydroxyanthraquinone (Alizarin) chelate polymer

(1) Direct condensation method:

The procedure was in accordance with that described previously for the preparation of base catalysed oxine polymer. A gel was not

produced, however, when resorcinol and formaldehyde were added to the alkaline solution of alizarin and formaldehyde. After curing at 110°C for two days an almost black solid was obtained. The solid was crushed in a mortar, and the 30-60 mesh size retained, and washed with water. The resin was Soxhlet extracted for 16 hours, washed with 0.1m-HCl and finally with water. The purple resin on washing with 0.1m-HCl changed colour finally producing a yellow solid. This yellow solid wassoluble in strongly alkaline solutions producing a purple coloured solution of Alizarin itself. The water washed resin was allowed to air dry and finally stored in a tightly sealed bottle.

(2) Azo coupling of Alizarin to polystyrene-divinylbenzene copolymer:

The techniques used in this preparation are similar to those previously discussed for both oxine and salicylic acid but using Alizarin in the same molar proportions. The resin was air dried and a crushed sample was thoroughly dried and microanalysis obtained.

D. (i) Preparation of 4-(2-pyridyl azo) resorcinol (P.A.R.)

The synthesis was essentially the reaction of 2-aminopyridine in sodium ethoxide with isoamylnitrite. The resulting diazo compound was allowed to react with resorcinol in alcohol. The red solid produced was washed with ether, and allowed to dry. An infra-red spectrum of the sodium salt was identical with that of a sample obtained from W. J. Geary[91], who supplied the synthetic procedure.

(ii) Azo coupling of P.A.R. to a polystyrene matrix:

The sodium salt of P.A.R. was allowed to react in an alkaline solution with the diazo derivative of polystyrene. This itself was obtained from the remaining portion of polyamino sytrene. The coupling, washing and sampling techniques were exactly the same as described for the previous polystyrene azo chelate polymers.

E. Preparation of condensation resins incorporating 4-Nitroso-Resorcinol as the functional molecule

Two such resins were prepared, one a 4-Nitroso-Resorcinol-formaldehyde polymer and the second a 4-Nitroso-Resorcinol-formaldehyde phenol copolymer. The phenol in the latter was in an equimolar ratio to 4-Nitroso-Resorcinol i.e. 0.20 moles. The procedure was identical with that described in preliminary stages of 2(b). The ground samples were screened as previously explained, and the appropriate portions Soxhlet extracted with ethanol for 16 hours. The samples were washed with 0.1M-HCl and finally with deionised water. The resins were air dried and retained in sealed bottles. Samples of dried material were submitted for elemental microanalysis.

F. Estimation of amino groups in chelate ion exchange resins

An approximate weight of the resin was dried in a vacuum desiccator over phosphorous pentoxide for two weeks. A known weight of the resin containing an estimated 0.3-0.4m moles of titratable nitrogen was equilibrated with a known volume of N/10 perchloric acid in glacial acetic acid and approximately 30 ml of glacial acetic acid at 90-100°C. The reaction vessel was securely stoppered to prevent evaporation of the solvent. The

sample was allowed to equilibrate undersuch conditions for 60-65 hours. The resin was then filtered off and washed with 70 ml of hot acetic acid. Two drops of 0.5% Crystal Violet indicator were added to the combined filtrate and washings and the solution was back titrated with 0.1m sodium acetate solution in glacial acetic acid. The perchloric acid 0.1N in glacial acetic acid was commercially available material from B.D.H. The sodium acetate, 0.1m in glacial acetic acid was prepared by dissolving 8.2g of anhydrous sodium acetate in 300ml of glacial acetic acid and diluted to 1 litre. The solution was standardized against perchloric acid (0.1N) in the same solvent. The stability of the perchloric acid solutions at 100°C were examined, and was found to be unaffected by heating at 100°C for 60 hours.

G. Estimation of the sodium-hydrogen exchange capacities

The sodium-hydrogen exchange capacities of the salicylate chelate ion exchangers were determined using two procedures.

(1) A weighed amount of the air dried resin was allowed to equilibrate with a sodium carbonate solution, of which the carbonate concentration was known. The resin and solution were periodically shaken for 18 hours at room temperature. The resins were filtered off, and washed with deionised water. The combined filtrate and washings was back titrated using a standardized hydrochloric acid solution and methyl orange was indicator. The sodium carbonate used was dried at 100°C for several hours and a sample titrated against the standard acid solution.

(2) The experimental procedure was similar but using a known volume of sodium hydroxide solution (Ca. 0.1m). The excess alkali and washings were back titrated after equilibration using phenolphthaleim

as indicator and standardized hydrochloric acid. The molarity of the sodium hydroxide solution was standardized against the hydrochloric acid using same indicator.

H. Determination of metal ion capacities of the prepared chelate-ion exchangers

(1) In acetate buffers (except uranyl (II) ion)

The procedure used by several workers was to allow a known quantity of resin (usually 0.50g or 1.00g) to equilibrate with a buffered metal ion solution, of known metal ion concentration. After equilibration the metal ion concentration of the solution in contact with the resin was determined. The disadvantages here however were that (1) large dilution factors are usually necessary before the metal ion concentrations can be determined (2) Precipitation of metal ions must be prevented during equilibration with the resin. Some workers, in particular Gregor[49] and co-workers, used different types of buffers, ranging from simple chloride to phthalate and phosphate buffers. The nature of the last two buffers will possibly affect the capacity of the resin, i.e. the complexing ability of phthalate and phosphate will be more pronounced than with chloride ions. The procedure adopted here was to use acetate "buffers", over the whole pH ranges to be studied. The buffers were prepared as follows:

pH value (± 0.1)	Buffer composition
6.80	2.0 mole of sodium acetate, and 40 ml of 1m acetic acid diluted to 2 litres.
5.6	2.0 mole of sodium acetate and 25 ml of glacial acetic acid diluted to 2 litres.
4.3	1.7 mole of sodium acetate and 320 ml of glacial acetic acid diluted to 2 litres.
3.6	0.45 mole of sodium acetate and 350 ml of glacial acetic acid diluted to 2 litres.
2.7	0.013 mole of sodium acetate diluted to 2 litres with 2M-acetic acid.

The 0.2M- metal ion solutions were prepared from the following laboratory grade reagents:

Copper	using	$Cu(NO_3)_2.3H_2O$
Nickel	"	$NiCl_2.6H_2O$
Cobalt	"	$CoCl_2.6H_2O$
Zinc	"	$ZnSO_4.7H_2O$
Aluminium	"	$Al_2(SO_4)_3.16H_2O$
Uranyl	"	$UO_2(NO_3)_2.6H_2O$

The general method used to estimate total capacities of various metal ions was as follows:-

To 25.0ml of the appropriate buffer, 25.0ml of the metal ion solution was added. The bottle was stoppered tightly and the contents shaken, the pH of this solution was obtained using a PYE, model 292, pH meter, which had been previously standardised against pH 4.00 and pH 9.20 buffers. Exactly 1.00 grm of the air dried resin (not previously conditioned by shaking with appropriate buffer) was allowed to equilibrate for 48 hours with constant shaking. The pH of the final solution was measured on the same instrument, and the resin filtered off using a No.3 or 4 sintered glass crucible. The resin and crucible were washed with a 10% v/v solution of buffer until the washings were metal ion free. The metal was eluted from the resin using approximately 40ml of 4fm-HCl. The metal chloride solution was filtered off, the resin and filter paper were washed with fm-HCl.

The filtrate and washings were diluted to the mark with deionised water. The concentration of the metal ion was determined using the following colorimetric methods and a UNICAM SP 500. Cobalt was determined using thiocyanate/acetone[92], nickel using dimethylglyoxime[92], copper using diethyldithiocarbamate in $CHCl_3$[93], zinc using 5-(O-carboxylphenyl)-1-(2-hydroxy-5-sulphophenyl)-3 phenylformazan (Zincon)[94] and aluminium using 8-hydroxyquinoline in $CHCl_3$[12]. The validity of this method was established by using an approximately 0.004fm solution of cobalt metal ion/acetate buffer solution and determining the initial and final concentrations of cobalt. The resin was washed and the cobalt eluted as described previously. The two capacities were found to be in good agreement i.e. less than 5% error.

The used portions of resin were stored in sealed bottles containing distilled water. When required the resin was filtered off and washed with deionised water until chloride free. The exchanger was allowed to air dry and stored in stoppered bottles. To ensure that no detrimental effects had occurred during recyclisation, the cobalt capacity (at a known pH) was redetermined. This procedure was used for all the resins and after each cyclisation.

(2) In citrate buffers (for uranyl (II) ion only):

A 0.2m solution of uranyl nitrate was prepared from a laboratory grade $UO_2(NO_3)_2.6H_2O$. For capacity determinations it was necessary to use a citrate buffer, as uranyl ions were precipitated above pH 4.5. The citrate buffer was prepared from molar citric acid and the pH adjusted with either nitric acid or ammonia solution. The capacities were determined as previously described, but washing with the appropriate citrate buffer. The variation of ionic strength of the citrate/uranyl solution was negligible. The uranium concentration of the elutent was determined using 8-hydroxyquinoline[93] and the SP500. Using 50 mls of 0.1m uranyl nitrate solution the capacities of the resins were determined to observe the effect citrate had on metal ion uptake, over the pH range 1.0 to 4.0.

I. Determination of rate of equilibration of metal ions with chelate ion-exchangers

From the determinations carried out in section (H) it was possible to calculate the total capacity of each resin, at a specific pH. This capacity expressed in m moles (say x) was

used to investigate the rates of equilibration of metal ions with the resins. The procedure adopted for copper was:- 100ml of a solution containing 50 ml of acetate buffer and 2x m moles of copper nitrate, were shaken for 30 seconds and the pH checked. Exactly 1.00 grm of air dried resin was allowed to equilibrate with the solution for 30 mins. with constant shaking. The pH of the solution was measured and the resin filtered off. Washing techniques and elution of copper ions from the resins were as described previously. The concentration of copper absorbed on the resin was determined using the standard procedure. The room temperature during equilibration was noted, and the whole procedure repeated using varying increments of time. The pH's of the solution after equilibration were relatively constant $\pm$ 0.2 pH unit. The rate of equilibration for Cu(II) ions was determined for all 15 samples of prepared exchangers. The 4 exchangers derived from polystyrene-divinylbenzene copolymer were investigated further to evaluate uranyl rate of equilibration. Using the same procedure as outlined above but this time 2x m moles of uranyl nitrate only in 100 mls of deionised water at a specific pH was used. Washing techniques involved using deionised water only, and again the temperature of equilibration was obtained. The final pH's of the solutions were relatively constant $\pm$ 0.2 pH units.

J. <u>To determine the influence basic eletrolytes and acetic acid have on metal ion capacities</u>

The metal ion chosen was uranyl, since the maximum capacity occurred within the natural pH range of uranyl nitrate solutions. Therefore, no buffers were necessary as pH variations of the final solution were small ($<$ 0.3 pH units). The systems studied were:-

$UO_2(NO_3)_2/NaNO_3$

$UO_2(NO_3)_2/NaCl$

$UO_2(NO_3)_2$/acetic acid

$UO_2Cl_2/NaCl$

and $UO_2(Acetate)_2$/acetic acid

However, the last system did prove difficult as the final pH values differed by one pH unit, and had to be adjusted to a constant pH using alkali. The method involved using 2x m moles of uranyl nitrate in 100 mls of 0.01m solution of say sodium nitrate. The usual method of determining the capacities was employed. The procedure was repeated using 0.05, 0.10, 0.50 and 1.0m solutions of sodium nitrate. This was repeated for NaCl and acetic acid with uranyl nitrate, NaCl with uranyl chloride and uranyl acetate with acetic acid.

K. To evaluate the effect of varying metal ion concentration on the total capacity

The initial system studied was uranyl nitrate solution of 0.05 and 0.10 molar concentrations. The capacities were determined as previous using 50 mls of the uranyl solutions and 1 grm of resin. The pH's of the final solutions were relatively constant (variation less than 0.2 pH units). This evaluation was repeated using the same concentration of uranyl solutions, but maintaining a constant ionic strength of 0.50 using $NaNO_3$ at approximately the same pH value. The uranyl capacities of the resins were redetermined using 0.05 and 0.10 molar solutions of uranyl chloride (50 ml) and also for 0.05m solution (50 ml) of uranyl acetate. Variations in the final pH values were overcome by using a relatively constant initial pH value. This in turn was achieved by the addition of dilute

alkali or acid to the system. This procedure was certainly applicable to the determinations discussed in sections J and K.

L. Determination of uranyl capacities from solutions containing the $Na_4UO_2(CO_3)_3$ complex

Several workers[81,95] have established that uranium occurs in trud solution in sea water as the tricarbonato complex $UO_2(CO_3)_3^{4-}$. The uranium concentration is remarkably constant (3.34 ug/l)[96], only second-order variations occurred between samples obtained from the Atlantic and Pacific oceans. Uranium tricarbonato complexes were prepared from UO_2Cl_2, $UO_2(NO_3)_2$ and UO_2(acetate)$_2$ in the following manner:

(1) $Na_4UO_2(CO_3)_3$ from uranyl nitrate and sodium carbonate.

The uranyl salt (0.02m) was dissolved in 100 ml of deionised water and sodium carbonate (0.06m) added. The yellow saturated solution was diluted to 500 ml, and the flask agitated for 24 hours. The uranium concentration of the final solution (filtered solution) was determined and the pH value noted. This preparation was repeated using the same molar concentrations for uranyl chloride and uranyl acetate. Exactly 50 mls of these saturated uranyl tricarbonato solutions were allowed to equilibrate with 1.00g of air dried resins. The procedure used was identical with that already outlined in section H(2), except the resins were washed with a dilute carbonate solution of the appropriate pH.

Two of the polystyrene-divinylbenzene chelate ion exchangers incorporating the salicylate and P.A.R. functional groups, were investigated further to ascertain whether pH affected the uranyl capacities. A borate buffer was prepared (only small pH changes

will occur in such buffers at pH's 7 to 9) as follows:- to 50 ml of 0.1m Boric acid and 5.0 mls of the uranyl tricarbonato complex solution (derived from UO_2Cl_2 and Na_2CO_3), potassium chloride was added so that the final solution on dilution would be 0.1m with respect to it. Varying quantities of a sodium carbonate solution were added to obtain the approximate ($\pm$ 0.1) pH. The combined solutions were diluted to 100 ml in a volumetric flask. The pH range covered after equilibration of 1.00 g. of air dried resin was 7 to 9. The uranyl capacities of the resins were determined using the standard techniques.

RESULTS AND DISCUSSION

Elemental analysis of direct condensation

Table 1 RESINS

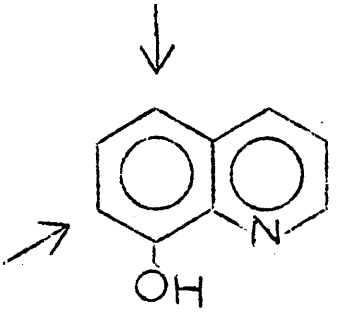
Resin	% Element		
	C	H	N
Oxine (base catalysed)	57.5	3.9	6.4
Oxine (acid catalysed)	68.9	4.8	4.2

From the analysis given in Table 1, thenumber of m. moles of chelating groups i.e. 8 hydroxyquinoline available per g. of resin can be deduced from the nitrogen content. This quantity is 4.6 m. moles and 3.0m. moles/g of resin respectively for the base catalysed and acid catalysed resins. These values in turn suggest that the total theoretical capacity of the resins for metal ions will be 4.6 and 3.0 m.moles accordingly, assuming a 1:1 complex is formed. The actual measured capacities of these two resins are very low, and in fact the results are contrary to previous theories, i.e. it would be expected that a lightly crosslinked resin would have a higher capacity than a highly crosslinked polymer. Thus the base catalysed resin should have a much lower capacity than the acid catalysed one.

Table 2

Resin	Metal ion	Capacity m.moles	Optimum pH
Base Catalysed	Co^{2+}	0.02	3.3 to 5.3
	Ni^{2+}	0.02	3.1 to 3.5
	Zn^{2+}	0.05	3.1 to 3.5
	Al^{3+}	0.02	> 4.7
	Cu^{2+}	0.05	3.5
Acid catalysed	Co^{2+}	0.01	3.2 to 3.7
	Ni^{2+}	0.005	3.2 to 3.7
	Zn^{2+}	0.01	3.2 to 3.8
	Al^{3+}	0.09	> 4.9
	Cu^{2+}	0.05	> 5.7

Although in general the base catalysed resin has higher capacities than the acid catalysed one, the highest capacity exhibited is for Al^{3+} by the acid catalysed polymer (Table 2). These extremely low results could be attributed to the high density of the resin which prevented penetration by the metallic ions. This could certainly be the case with the base catalysed ion exchanger, but is doubtful for the acid catalysed form. The reaction of oxine with formaldehyde produces numerous definite compounds depending on the reaction conditions. The structure of many of these condensation compounds have not been specified. The majority of condensation reactions with formaldehyde do however occur in the 5 or 7 position[16, 97].

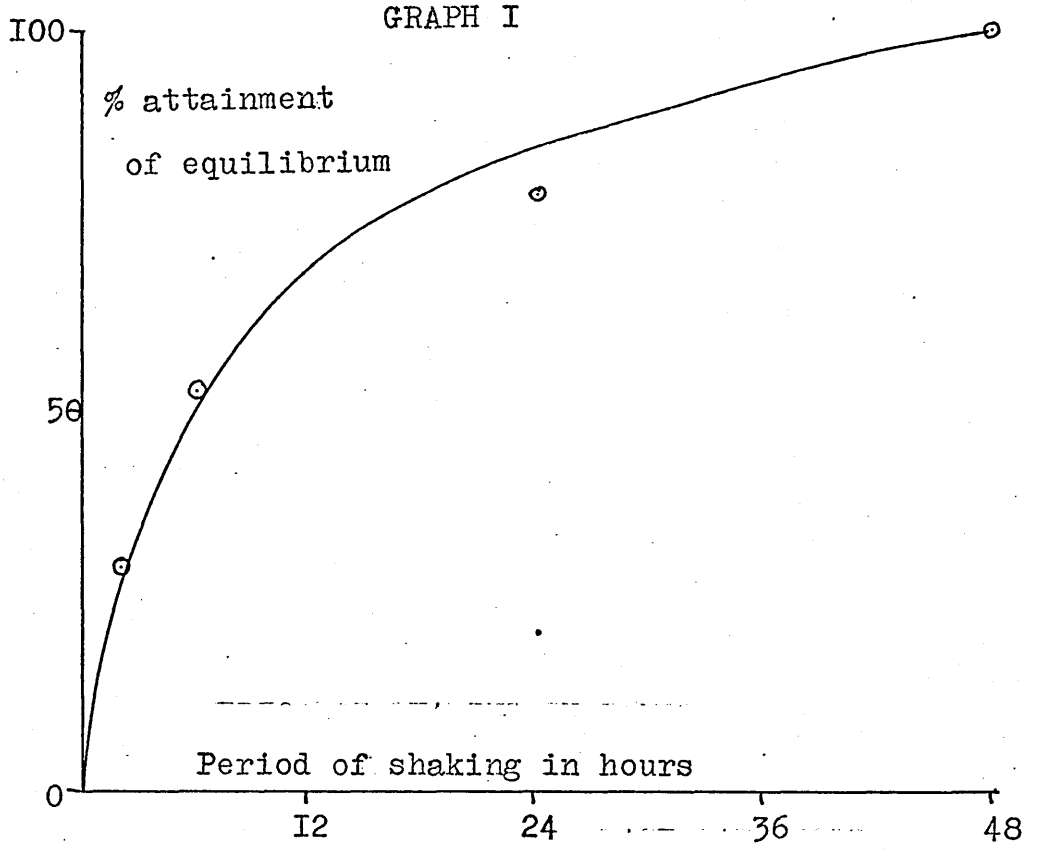


It may be possible that condensation occurred in the 7 position in both cases, thus causing steric hinderance of the chelating sites. The rate of equilibration of both resins for copper(II) ions was measured, but the kinetics were extremely slow, at least 36 hours were required before 90% attainment of equilibrium was reached (graph 1 and 2). The equilibration results are plotted as a function of time and % attainment of equilibrium. The latter variable is derived from assuming 100% equilibration of metal ion after 48 hours, any integers of this time are expressed as a percentage. These results are certainly in agreement with a heavily crosslinked network. The acid catalysed polymer prepared according to Degeiso's[39] procedure possibly resulted in the formation of a crosslinked resin as it is insoluble in both dioxan and dimethylformamide. Acid catalysis of oxine and formaldehyde usually results in the formation of a low molecular weight linear polymer.

The preparation of a condensation polymer incorporating 1, 2-dihydroxy anthraquinone (alizarin), produced a chelate ion exchanger of higher capacity than the oxine resins. Although the capacities are higher (Table 3, graph 3) the resin itself was unstable. Alizarin groups were leached out of the condensation matrix after each cyclisation (Table 4). This resin could be regarded as a

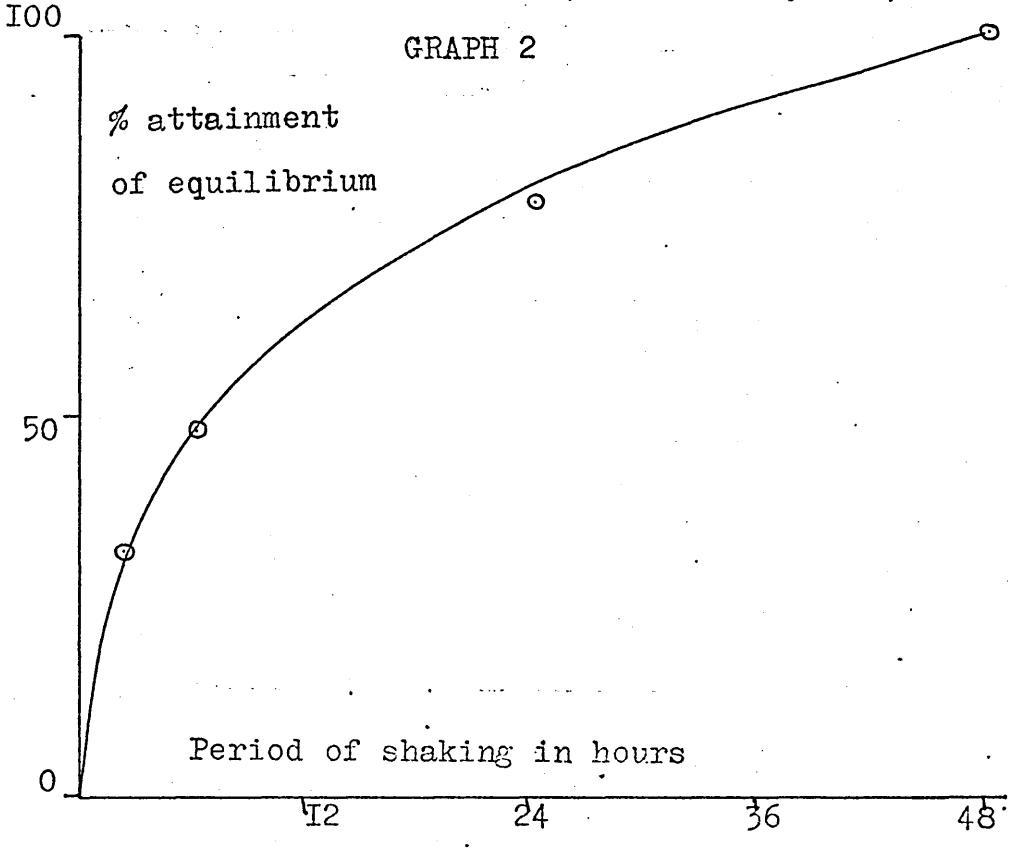
OXINE CONDENSATION RESIN(acid catalysed).

GRAPH I



OXINE CONDENSATION RESIN (base catalysed).

GRAPH 2



polymer matrix with the chelating compound trapped within it, i.e. Dauel and Hutschneker theory[53].

Table 3

Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	0.18	6.1
Ni^{2+}	0.08	6.0
Al^{3+}	0.02	4.6
Cu^{2+}	0.28	5.6
Zn^{2+}	0.09	6.0

Table 4

No. of Cyclisations	1	2	3	4
Co^{2+} capacity in m. moles	0.18	0.12	0.11	0.10
Appropriate pH	6.1	6.0	6.0	6.1
Corrected value from Graph 3	-	0.16	0.16	0.18

From Table 4, it is evident that after the first cyclisation 25% of the original capacity was lost due to the removal of chelating sites. The fourth cyclisation resulted in 45% of the capacity being lost due to leaching out of chelating groups. The loss of alizarim molecules was more evident when studying capacity measurements i.e. numerous coloured precipitates were obtained.

The colour of these precipitates depended on metal ion and pH of the solution. Little or no precipitates were obtained when rate of equilibration was being studied. It is possible that the loss of chelating sites is due to concentration of metal ion and pH of the solution. The values given in Table 3 and Graph 3 have not been corrected to account for the loss of capacity. The metal ions were studied in the sequence given in Table 3, therefore the zinc capacity should be nearly double the value quoted. The highest capacity will still be for cupric ions however with zinc and cobalt approximately equal. From the stability constant[98] of aluminium alizarin complex (monomer), which is of the order 10^{15}, it would be expected that this ion would have the highest capacity. This can be satisfactorily explained in terms of hydrated metal ion radii.(Table 5). Copper has the second smallest hydrated ionic size of the metal ions studied, whilst aluminium has the largest. This arguement would imply however that nickel ought to have the highest capacity, but it may be that Ni-alizarin complexes are relative unstable. As the resin becomes more porous, due to loss of functional chelating groups, this will tend to favour the larger hydrated ions, which forms more stable complexes with alizarin.

Table 5

Metal Ion	Al^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Na^{+}
Hydrated ion size ^{o}A	4.75	4.23	4.04	4.19	4.30	3.58

Values obtained from ref.99

Although the polymer would appear to be less dense than oxine resins, the rate of equilibration with cupric ions, was of the same magnitude as for the previous resins (Graph 4).

The salicylic acid polymer prepared by direct condensation methods, had sodium-hydrogen exchange capacities comparable with resins prepared by other workers[45]. The hydrogen capacity obtained using sodium hydroxide was approximately (within 5%) twice that obtained using sodium carbonate solution (Table 6). It is reasonable to assume therefore, that with sodium hydroxide both the carboxyl and hydroxyl hydrogen's have been replaced, but with sodium carbonate solution only the carboxyl hydrogen.

Table 6

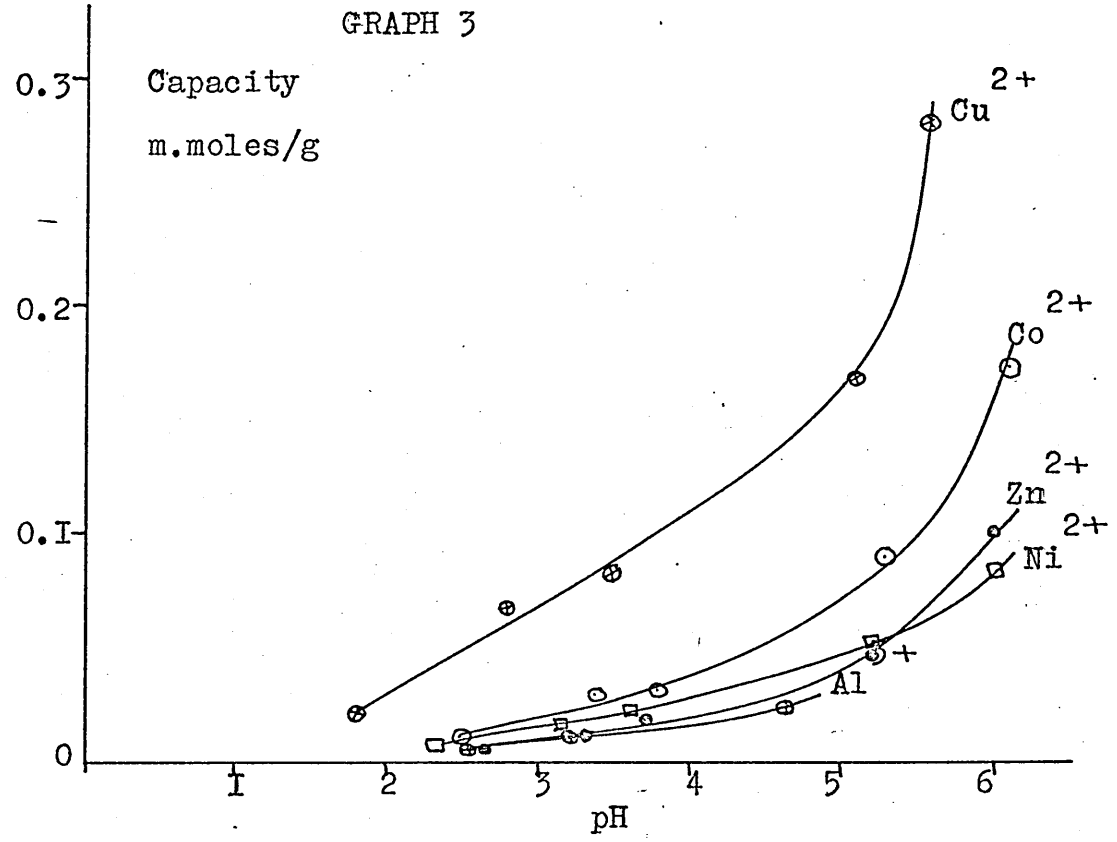
Sample No.	Capacity obtained from Na_2Co_3	Capacity obtained from NaOh
1	1.66	3.45
2	1.77	3.53

Values expressed in m.moles/g. of air dried resin

This implies that the total capacity for metal ions forming a 1:1 complex will be 1.71 (average). The highest measured capacity is however only approximately a third of this value and is for Co^{2+} at pH 5.7. Again from stability constants aluminium should have had a much higher capacity than was measured. The aluminium-salicylate complex has been reported to be stable having a stability constant of ca. 14.0[100]. The order of stability for salicylate complexes is Fe^{3+} $>Al^{3+}$ $>Cu^{2+}$ and Ni^{2+}, Co^{2+} and Zn^{2+} apparently forming complexes of equivalent stability

ALIZARIN CONDENSATION RESIN.

GRAPH 3



GRAPH 4

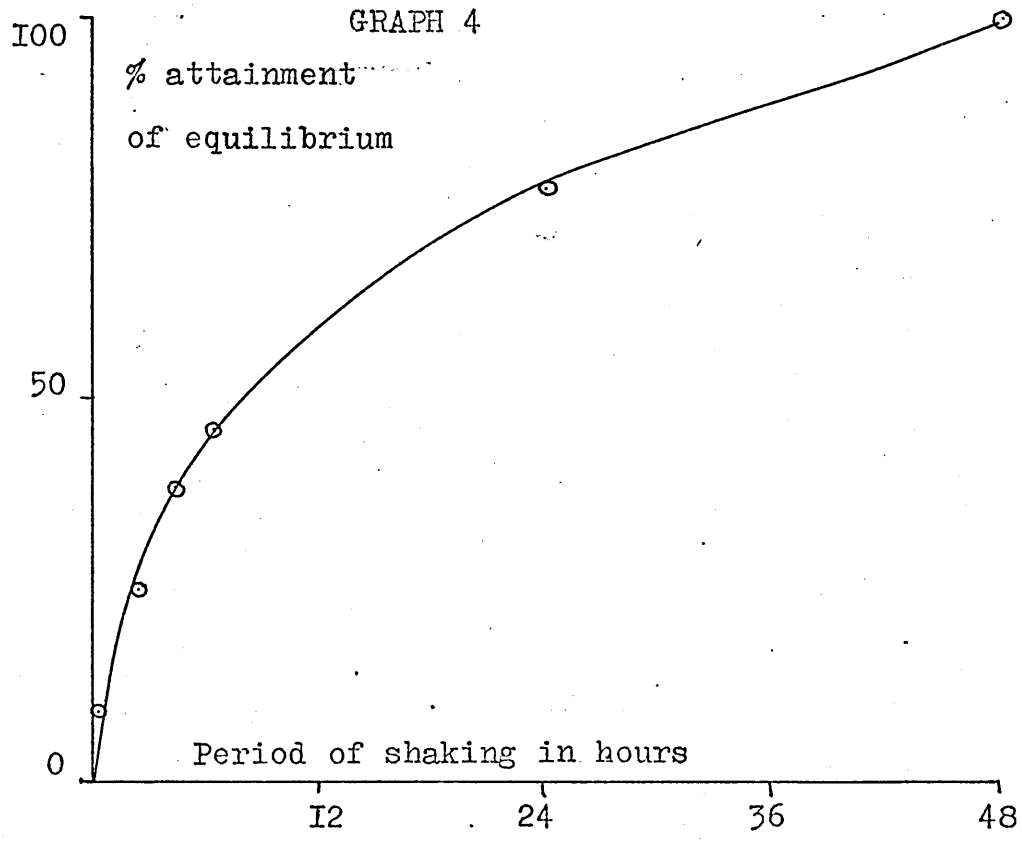
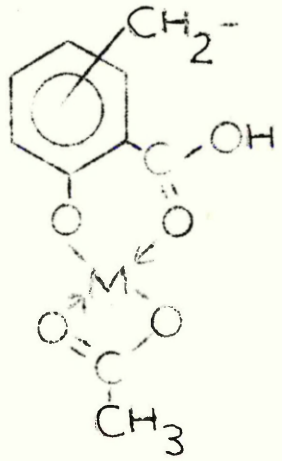


Table 7

Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	0.58	5.7
Ni^{2+}	0.10	5.7
Zn^{2+}	0.42	5.6
Al^{3+}	0.21	4.7
Cu^{2+}	0.50	5.5
U^{6+}	0.02	7.7

(Co^{2+} $K_{(1)}$ = 6.72 , Ni^{2+} $K_{(1)}$ = 6.95 and Zn^{2+} $K_{(1)}$ = 6.85[101]). The stability complex of copper-salicylate is $K_{(1)}$ = 10.64[103]. Although the stability constants vary from one paper to the next it is however generally accepted that the ratio of metal ion to salicylic acid varies according to the reaction conditions. It is unlikely however that the salicylic acid copolymer prepared can form these various metal ion-complexes. It is necessary to assume that the complexes are 1:1 and to obtain electron neutrality of the metal ion an acetate ion is attached to it thus:



when M is a divalent ion

The measured capacities suggest the order should be $Na^{+} > Co^{2+} > Cu^{2+} > Zn^{2+} > Al^{3+} > Ni^{2+}$. The position of all the metal ions studied in the above sequence can be explained in terms of stability constants correlated with solvated metal ion size, or alternatively the small differences in pH values at which maximum absorption values are quoted. However the difficulty arises in explaining the position of nickel (II). From solvated metal ion considerations, the metal ion aught to have the second highest capacity, but approximately equivalent to that of Co^{2+} and Zn^{2+} from stability constant considerations. The order for metal ions at pH 4.0 is $Al^{3+} > Cu^{2+} > Zn^{2+} \simeq Ni^{2+} \simeq Co^{2+}$, this sequence resembles that of the salicylic acid monomer and the metal ions, when studying stability constants only. It appears therefore that the solvated metal ion phenomena is only a secondary effect at this pH value. As the pH rises however the stability constant becomes less effective, giving preference to a resin effect which at the moment cannot be explained satisfactorily. This effect may be due to the formation of inter-salicylic acid chelates, which have been reported previously[103], but not with salicylic acid and acetic acid. The formation of mixed salicylic acid chelates generally have higher stability constants than the corresponding salicylic complex.

The capacity for uranyl ions is very low. 0.02 m.moles/g of resin at pH 7.7. This will certainly be due to the citrate buffer forming a complex with the uranyl ion. In general, citrate uranyl complexes are approximately twice as stable as the corresponding salicylate complex. In addition to this the size of the uranyl citrate complex will also govern the total U^{6+} capacity of the resin. The resin prepared however differs from that of

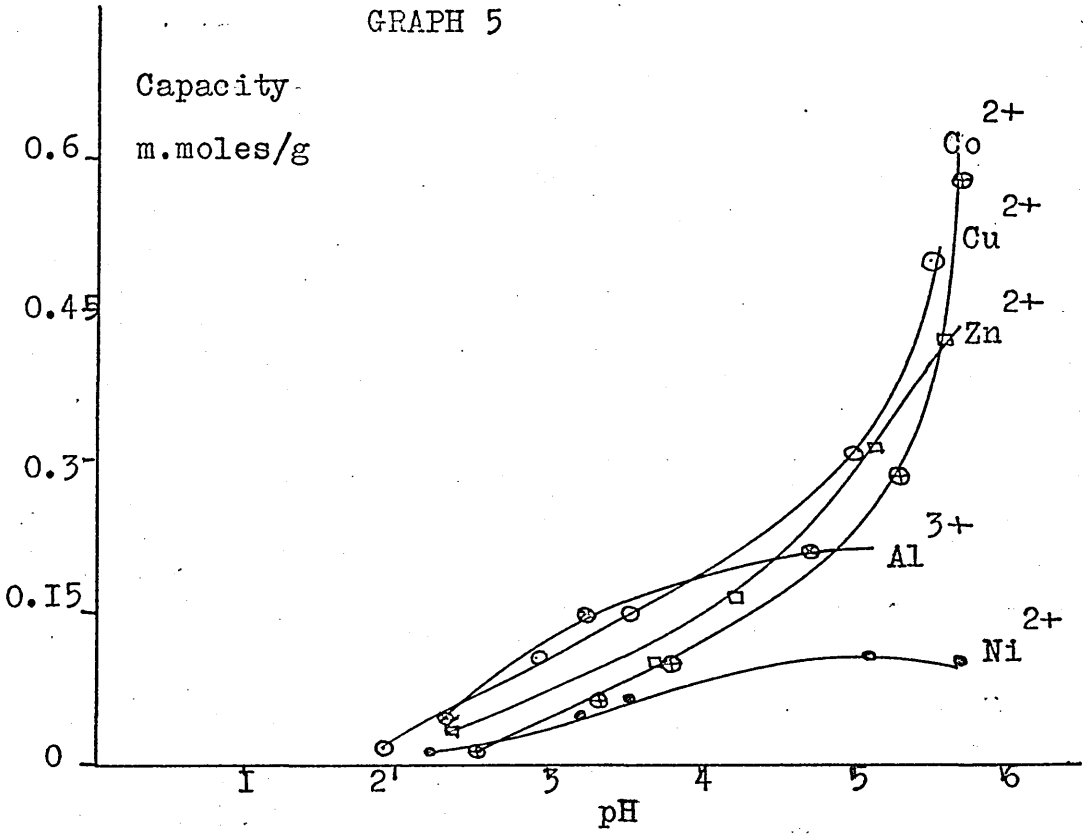
Degeiso's et al.[47], their resin showed a maximum sorption at pH 3.3. However the workers did not study the behaviour of uranyl ions above this pH, as chelation of uranyl ions in solution would be inevitable. The affinity for uranyl ions at this pH (3.3) of the salicylic acid polymer was very low, and over the pH range 1.5 to 7.0 the capacity was relatively constant. Although the capacities of the salicylate chelate exchanger are higher than the other three chelate exchangers discussed previously, the rate of equilibration is very slow. The rate in fact is slower than both oxine and alizarin chelate exchangers (Graph 6). This will be certainly due to a highly cross linked network, but may also be due to the stabilities of copper with respect to the chelate functional unit. The overall stability of the salicylate resin was very good, no decrease in capacity was observed on recyclising (Table 8).

Table 8

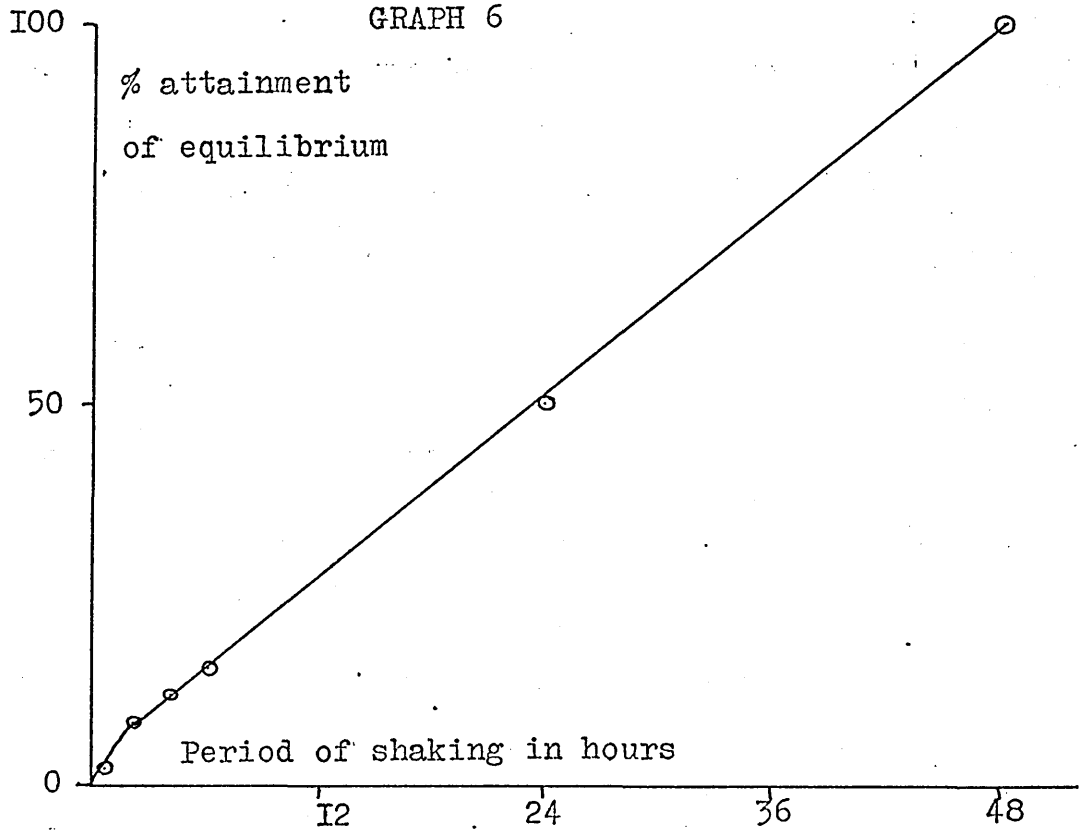
No. of Cyclisations	1	2	3
Co^{2+} capacity in m. moles	0.58	0.58	0.30
Appropriate pH	5.7	5.7	5.3
Corrected value from Graph 5	-	0.58	0.29

SALICYLIC ACID CONDENSATION RESIN.

GRAPH 5



GRAPH 6



From the microanalysis (Table 9) it was possible to calculate the number of m.moles of nitrophenol units/g. of resin. The number of m.moles of nitrogen/g. of resin was 0.86 or alternatively 0.86 m.moles of p-nitrophenol units. During reduction the total nitrogen content remains constant, but the % conversion of nitro to amino was 84, i.e. 0.14 m.moles of nitro groups remaining. The % conversion was derived from the total nitrogen content which was due to amino and nitro units, and from the titratable nitrogen which was due to amino units only.

Table 9

Resin	% element		
	C	H	N
p-nitrophenol-form aldehyde phenol	71.6	5.2	1.2
p-aminophenol-form aldehyde phenol	70.6	5.2	1.2
p-azophenol, oxine-formaldehyde phenol	64.4	4.0	3.3

Titratable nitrogen content of p-aminophenol-formaldehyde phenol copolymer 0.72 m.moles of nitrogen/g. of resin.

The amino content for the resin is 0.72 m.moles and the peroentage conversion of this derivative to the azo-oxine was 92%. This conversion factor is derived by assuming 100% conversion to the azo-oxine unit, and knowing the total nitrogen content, and nitro units remaining (difference between total m.moles of nitrogen less amino content for reduction step). If say the total nitrogen content is y, and let x be the nitro units remaining, then (y-x) will be equal to the nitrogen content due to azo-oxine units. Since the amino content of the resin is also known sa z, then for 100% conversion of amino to azo-oxine.

$z = 3(y-x)$ m.moles of nitrogen

This 100% conversion is never obtained, so that the % value will be expressed by

$$\frac{(y-x)}{z} \times 100$$

Hence one can obtain a % value for the conversion and therefore it is possible to deduce the amino content remaining. This resin had the following composition:-

0.14 m.moles of nitro groups/g. of resin

0.06 m.moles of amino groups/g. of resin

0.72 m.moles of oxine groups/g. of resin

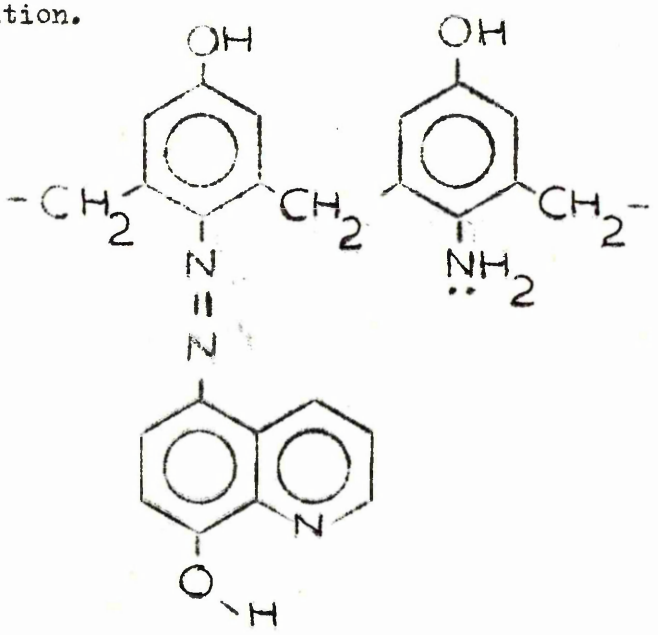
From this calculation the maximum capacity of the resin must be 0.72 m.moles of metal ion/g. of resin, assuming a 1:1 complex is formed. From Table 10 the maximum measured capacity was for copper having a value of 1m.mole/g.

Table 10

Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	0.58	6.1
Ni^{2+}	0.31	5.1
Cu^{2+}	1.00	5.9
U^{6+}	0.01	1.5

It is evident therefore that other groups are present within the resin matrix capable of bond formation with metal ions. It was first suggested that the remaining nitro units could be co-ordinating the metal ions, since p-nitrophenol complexes are known. This argument was rejected since the measured capacity of the nitro phenol polymer was 0.07 m.moles of Co^{2+}/g. of resin.

A second explanation was that the remaining amino units were acting like an anion exchanger. This was unlikely however as the pH of the measured metal ion capacities for the p-azo-phenol oxine resin were 5.9 to 6.1 and the theory was proved to be invalid as the resin had a capacity of only 0.05 n.mole of Co^{2+}/g. of resin. The final suggestion is that the azo units of the azo oxine functional group are "co-ordinating" the copper ion, thus giving rise to this extra capacity. This may not be possible however as there are insufficient amino units to produce this extra capacity (assuming "co-ordination" occurred via azo bond and amino unit), and the -OH of the phenol molecule is too far removed to participate in bond formation with metal ions and the azo linkage, thus OH cannot stabilise bond formation.



No satisfactory explanation can be postulated at present. All the other metal ions have capacities well within the theoretical value. From graph 7 if the order of stability is related to

the capacity, assuming solvated metal ion radii to have little or no effect, then at pH 5 the stabilities of the metal-oxine resin are of the order $Cu^{2+} > Co^{2+} = Ni^{2+}$. This series is identical with that of the stabilities of metal oxinates.

The capacity for uranyl (II) ions was low prticularly when citrate buffer was present (Table 10). The optimum pH condition when citrate was present for the maximum uranyl capacity was 1.5, and on increasing the pH to 4.3 the capacity decreased. When citrate was absent however the optimum pH for maximum capacity was 4.3, and decreased as pH tends to 1.0 (Table II). This low capacity for uranyl when in "buffered" solutions is undoubtedly due to the citrate present, and at low pH's the equilibrium lies in favour of the resin, whereas on increasing pH the uranyl citrate system is favoured.

Table II

System	Capacities for U^{6+} in m. moles		
0.1m Uranyl nitrate solution only	0.01 (2.0)	0.02 (3.4)	0.03 (4.3)
0.1m Uranyl nitrate solution + citrate buffer	0.01	0.01	0.01

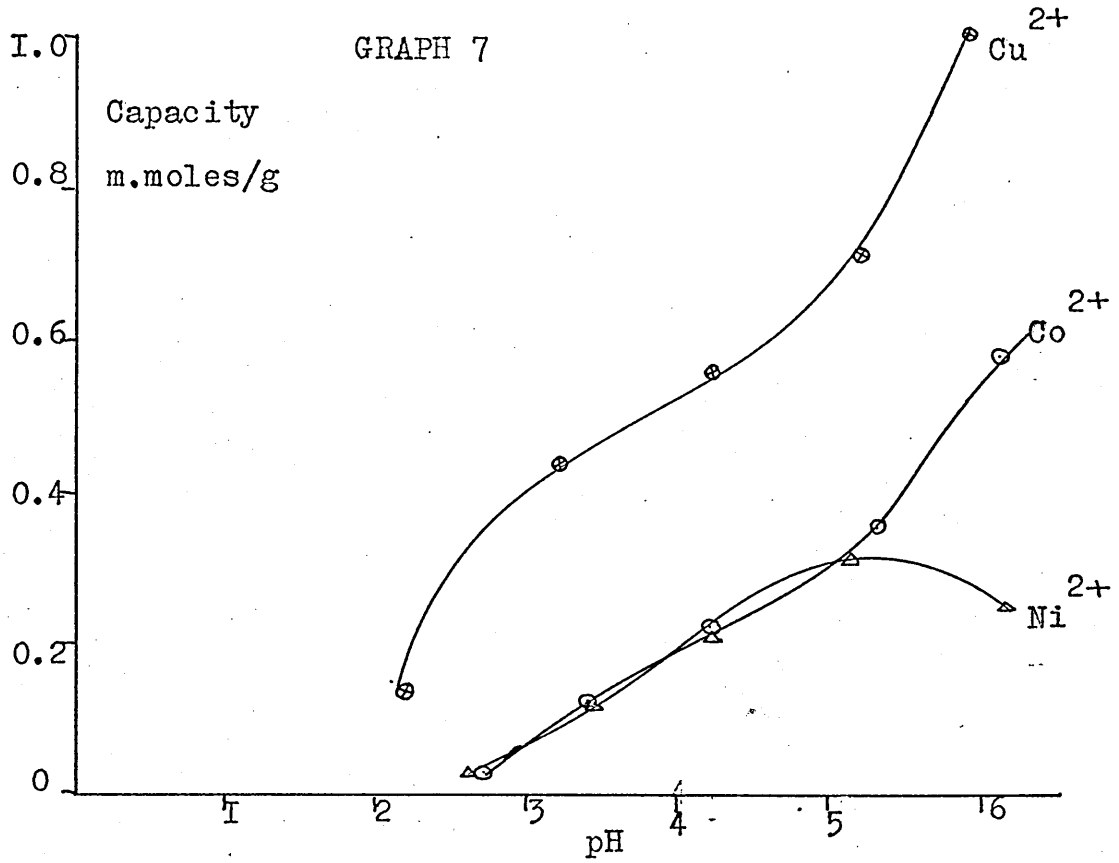
pH values in brackets

The behaviour of the resin with uranyl as pH increases i.e. capacity increasing, is analogous to the oxine monomer itself when employed in solvent extraction procedures. Generally higher pH's favour oxine extraction of uranyl (II) ions.

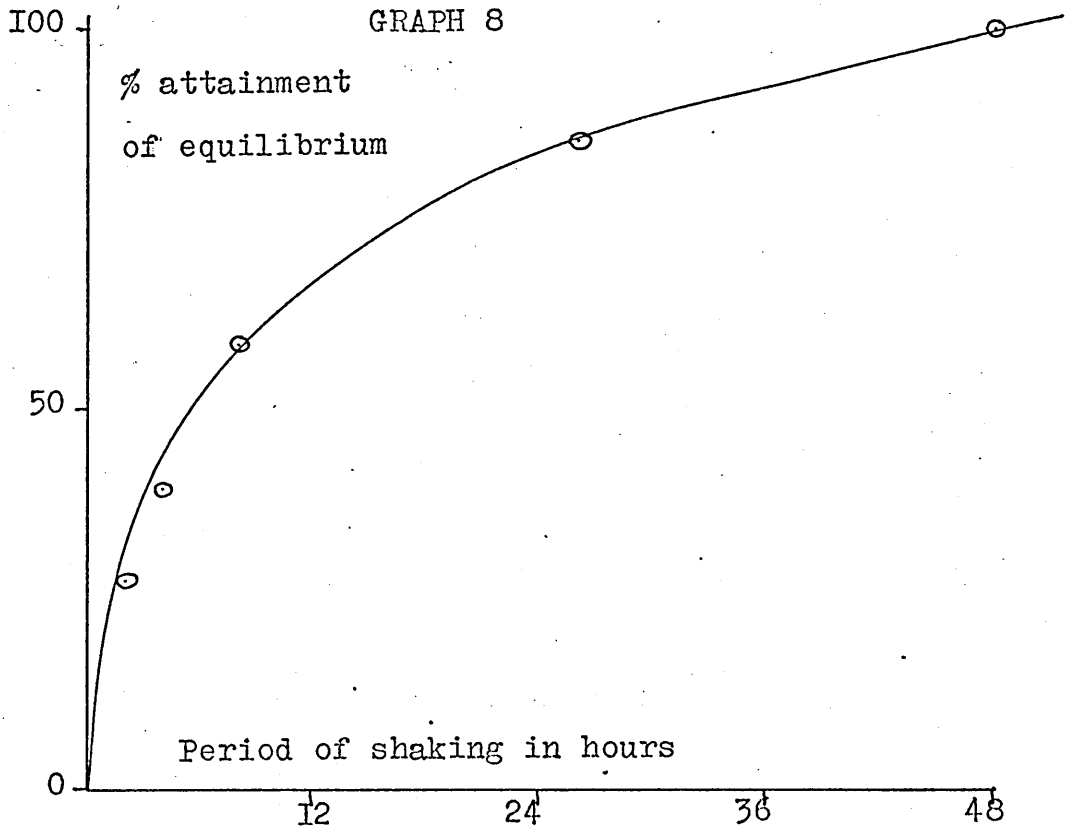
The kinetics of the p-azophenol-oxine resin (Graph 8) are very similar to the previous condensation resins prepared. The

P- AZO-PHENOL OXINE RESIN.

GRAPH 7

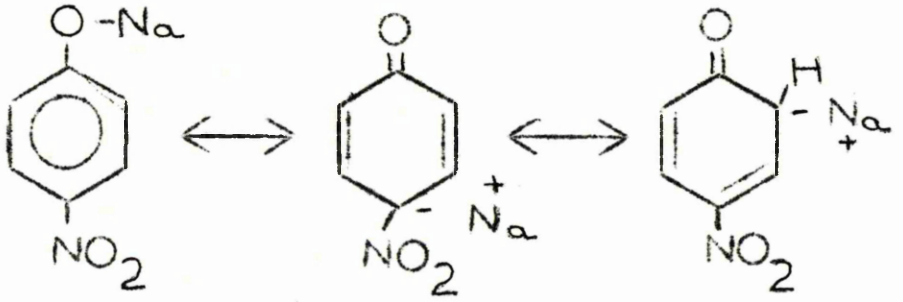


GRAPH 8



slow kinetics are unlikely due to a highly crosslinked matrix, as the capacities are favourable. It may be due to the rate of attainment of equilibrium being dependent on metal ion concentration.

Unlike the previous chelate ion exchanger derived from p-nitro-phenol, the 4-nitroso-resorcinol unit should be capable of self-crosslinking. Parrish[37] used o-nitro-phenol and resorcinol to prepare a chelate ion exchanger. It is true that these reagents will condense with formaldehyde to give a polymer, when only the theoretical quantity of base catalyst is present. In order to condense phenol and p-nitrophenol with formaldehyde, three times the theoretical quantity of base is required. This may be due to the formation of the nitrophenoxide ion thus



which would be resonance stabilised, and may propagate the reaction between the ion, phenol and formaldehyde. The quantity of base catalyst however for condensation of 4-nitroso-resorcinol and formaldehyde is the theoretical amount. This will certainly be a result of two activiating -OH groups largely outweighing the slightly deactivating -NO group. The net result is an activiated molecule, unlike p-nitrophenol which will be inactive or slightly deactivated.

Table 12

Microanalysis of 8-hydroxyquinoline resins derived from 4-Nitroso-Resorcinol polymers

Resin	% element		
	C	H	N
4-Nitroso-Resorcinol-formaldehyde	56.0	3.9	7.7
4-Amino-Resorcinol-formaldehyde	51.9	3.8	5.8
4-Resorcinol-formaldehyde azo-oxine	53.0	3.8	6.8
4-Nitroso-Resorcinol-formaldehyde phenol copolymer	63.9	4.4	4.2
4-Amino-Resorcinol-formaldehyde phenol copolymer	59.7	4.8	3.5
4-Resorcinol-formaldehyde phenol azo-oxine copolymer	62.2	4.3	4.6
4-Nitroso-Resorcinol-formaldehyde phenol copolymer	59.4	4.1	6.1
4-Amino-Resorcinol-formaldehyde phenol copolymer	53.0	4.0	4.9
4-Resorcinol-formaldehyde phenol azo-oxine copolymer	57.5	4.0	6.3
4-Nitroso-Resorcinol-formaldehyde phenol copolymer	61.1	4.1	4.6
4-Amino-Resorcinol-formaldehyde phenol copolymer	58.2	4.3	4.0
4-Resorcinol-formaldehyde phenol azo-oxine copolymer	62.0	3.9	5.1

Acknowledgement

The microanalyses quoted in this thesis were determined by J. Jordan L.R.I.C., Chemistry and Applied Chemistry Department, Salford University. The author wishes to express his appreciation for this valuable service.

From the analysis (Table 12), it is possible to calculate the number of m.moles of 4-nitroso-resorcinol units/g. of resin. These resins for future reference will be designated 1,2, 3 and 4 respectively, the order of notation corresponding to that of Table 12. The number of m.moles of nitrogen/g. of resin for resin No.1 is 5.5 or alternatively 5.50 m.moles of 4-nitroso-resorcinol units. During reduction however 1.4 m. moles of nitroso units were lost, and the percentage conversion to the amino is 67.0%. This figure is obtained as previously explained for p-nitrophenol-formaldehyde phenol copolymer. The assumptions made however are that any units in the resin formed as a result of incomplete coupling of oxine to the 4-diazo resorcinol unit do not contain nitrogen.

Table 13

Non aqueous titration values

Resin No.	m.moles of nitrogen due to amino unit/g. of resin
1	2.3
2	1.9
3	1.1
4	1.7

The numerical data obtained using the previous calculations are given in Table 14.

Table 14

Resin No.	Nitroso units m.moles /g. of resin	%reduction	Amino units m.moles /g. of resin	% azo coupling	Oxine units m.moles /g. of resin
1	1.4	67	2.0	42	0.5
2	0.6	76	1.4	47	0.4
3	2.4	32	0.8	63	0.5
4	1.1	62	1.3	48	0.4

In order to check the validity of the calculation, cobalt capacities were determined on all four, nitroso-resorcinol polymers and the corresponding amino derivatives. The cobalt capacities obtained and the % conversion of nitroso to amino are given in Table 15.

Table 15

Resin No.	Co^{2+} capacity m.moles /g. of resin		% conversion
	Nitroso	Amino	
1	1.28	0.56	44
2	0.60	0.29	48
3	1.08	0.56	52
4	1.03	0.54	53

These cobalt capacities were measured at pH 5.5 to 5.6.

Although these values are not in good agreement with values calculated (Table 14), the pH at which these values were obtained is not the optimum pH condition. From the calculated nitroso units remaining (Column 2 Table 14), assuming a 1:1 complex, the m.moles of metal ion these units can co-ordinate with are 1.4, 0.6, 2.4 and 1.1 for resins 1,2,3 and 4 respectively. The measured capacities are 1.28, 0.6, 1.08 and 1.03 respectively. With the exception of resin No.3, the rest are in good agreement.

From theoretical considerations the total capacities for metal ions are 1.9, 1.0, 2.9 and 1.5 m.moles/g. of resin for resins 1,2,3 and 4 respectively. These values compare favourably with capacities given in Tables 16, 17, 18 and 19 respectively.

Table 16

Resin No.1

Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	1.48	5.6
Ni^{2+}	1.45	5.7
Cu^{2+}	1.51	5.4
U^{6+}	0.07	1.3

Table 17

Resin No.2

Metal Ion	Capacity m.moles	Optimum pH
Co^{2+}	0.88	5.8
Ni^{2+}	0.63	5.9
Cu^{2+}	0.84	5.6
U^{6+}	0.02	1.3

The efficiency of the resin can be calculated from the measured and theoretical capacities. These values, as percentages of the total sites accommodated by metal ions are 80, 88, 63, and 90 for resin 1,2, 3 and 4 respectively.

Table 18

Resin No.3

Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	1.32	5.40
Ni^{2+}	1.38	5.60
Cu^{2+}	1.82	5.3
U^{6+}	0.06	2.0

Table 19

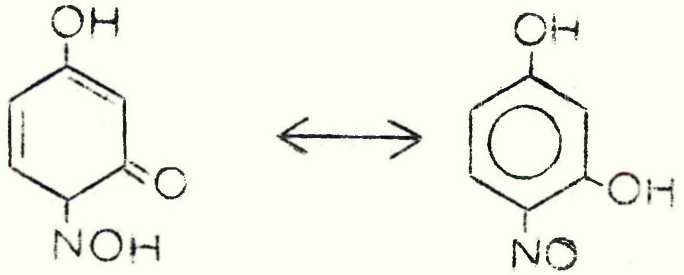
Resin No.4

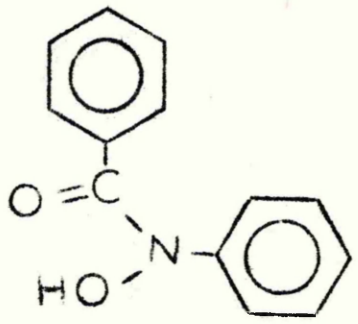
Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	1.12	5.5
Ni^{2+}	1.30	5.6
Cu^{2+}	1.45	5.4
U^{6+}	0.05	1.9

The difference in cobalt capacities for the nitroso resins and the corresponding resin coupled by an azo linkage to oxine should indicate the number of oxine units/g. of resin. These values must be taken at the same pH, and values for azo-oxine resins are obtained from graphs 9, 11, 13 and 15 accordingly. These values are resin No.1, 0.2; No.2, 0.25; No.3, 0.24; No.4, 0.10. These values do not check with the previous values calculated (Table 14), however from Table 1, nitrogen is lost during reduction ile. nitroso units are possibly leached out of the resin. This loss

would be adequate to account for the above discrepancy. The loss of nitroso groups appears to be a function of the resin, the more heavily crosslinked resin (No.2) lost only 0.49 m.moles/g. whereas resin No.1 lost 1.35 m.moles/g. Resins 3 and 4 have values of 0.84 and 0.47 respectively. The recalculated values for oxines units (in m.moles/g.) for resins 1, 2, 3 and 4 are 0.45, 0.38, 0.42 and 0.33 respectively. These values are comparable with the theoretical ones, given in Table 14.

The difficulty now appears to be explaining why the reduction step of nitroso units to amino units is unfavourable. A possible explanation of this is that 4-nitroso-resorcinol forms stable complexes with stannous or stannic salts. Other metallic complexes of 4-nitroso-resorcinol have been previously reported[104] particularly for copper (II) and cobalt (III) ions. The red cobaltic complex has the formula $(C_6H_5O_3N)_3Co$, and the copper ion produces a complex having the formula $(C_6H_5O_3N)_2Cu$. The formation of tin complexes is achieved only from stannous salts and 4-nitroso-resorcinol. Stannic salts do not produce a complex immediately but on standing for several days in an air tight container a precipitate is produced. The behaviour of 4-nitroso-resorcinol with tin salts is analogous to that of N-Benzoyl phenyl hydroxylamine[105]. This reagent forms stannous complexes having the composition $(C_{13}H_{11}O_2N)_2SnCl_2$. When stannic salts are present they initially undergo reduction to the divalent salt, followed by the formation of an addition compound. It is possible therefore that 4-nitroso-resorcinol exists in tautomeric forms.





N - Benzoyl, phenylhydroxylamine

The behaviour of these two reagents however is comparable only in their reactions to stannic salts. 4-nitroso-resorcinol forms different stannous complexes depending on the ratio of metal ion to chelating agent.

The 4-nitroso-resorcinol prepared according to Henrich's method had a composition favourable to that of the theoretical value

Found 40.60%C; 2.28%H; 7.82%N; 22.3%K

Theoretical 40.73%C; 2.26%H; 7.91%N; 22.1%K.

The tin complexes of 4-nitroso-resorcinol vary in colour from violet to green, they are readily soluble in dilute alkaline solutions, producing coloured solutions. Depending on the tin content, the complexes are insoluble in ethanol or ether.

The measured capacities of the 4 resins, are generally in good agreement with the proportion of 4-Nitroso-Resorcinol used. Resin 1 should have had the highest capacity, in fact it is resin 3. This is undoubtedly due to the low conversion during the reduction step of nitroso to amino. Resin 1 however has a higher

capacity than 4 which in turn is higher than 2. The order of capacities is therefore 3 > 1 > 4 > 2. From the measured capacities it would appear that hydrated metal ion size, has little or no effect, and that the stabilities of the copper, cobalt and nickel complexes of 4-nitroso-resorcinol should be approximately equal. The copper complexes might have a slightly higher stability, but no actual measurements of stability constants for these complexes have been reported. Probably the closest example is 1 Nitroso-2-naphthol, the order of stability of these complexes is Cu > Co > Ni, but the values are very similar[106]. This sequence would certainly be true for resins 1 and 4 and partially correct for 2 and 3.

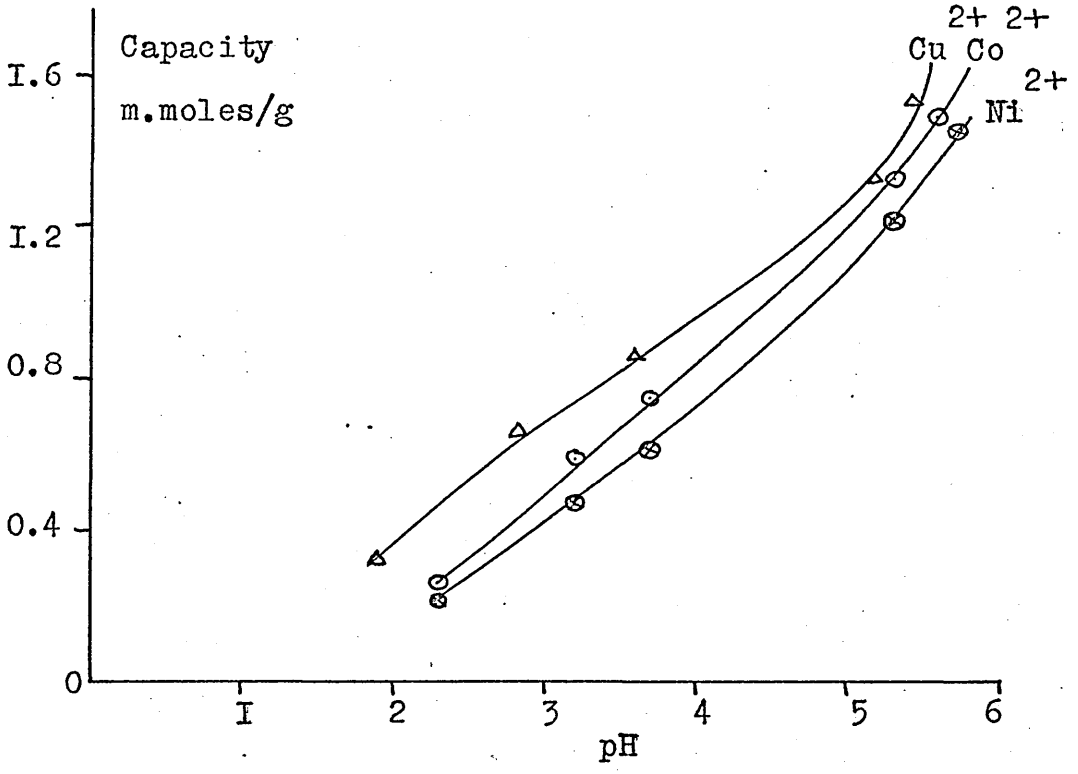
The uranyl capacities for these resins were low, (Graphs 17 and 18) when determined from solutions (1) containing citrate buffer and (2) when citrate was absent. These low capacities for all four resins cannot be satisfactory explained, as there are too many chelating sites within the resin.

A predominant factor will be the size of the hydrated uranyl species.

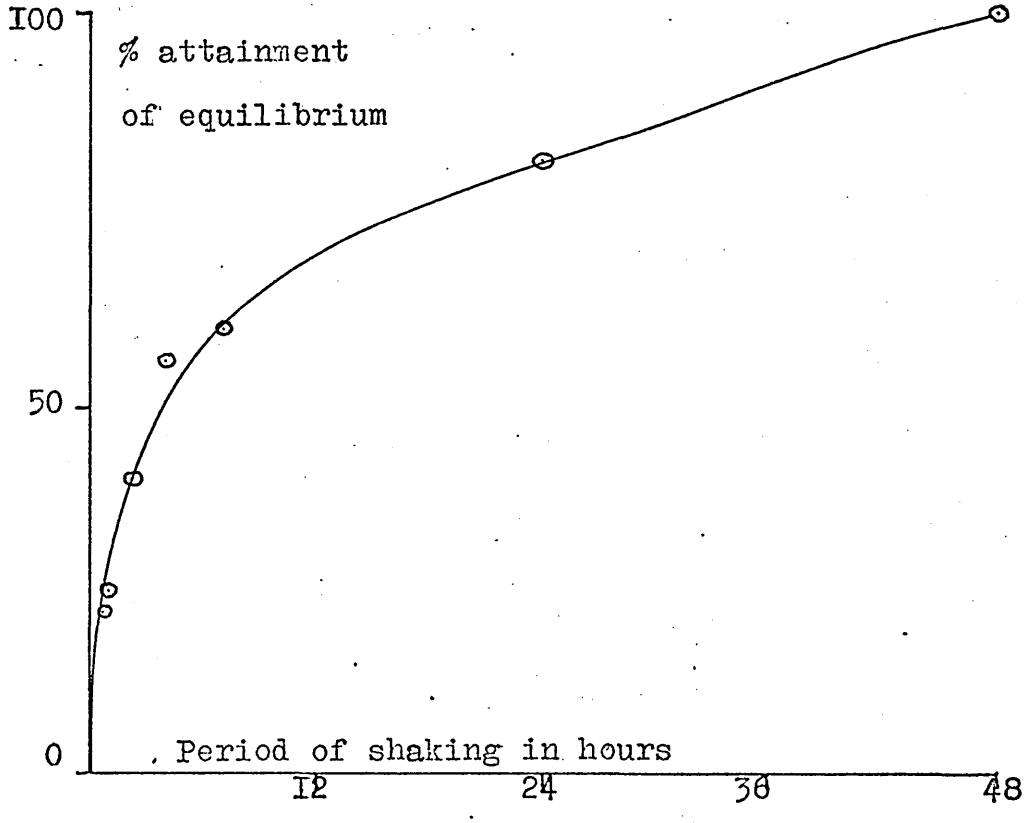
The rate of uptake of all four resins is slow (graphs 10, 12, 14 and 16), at least 30 hours are required to reach 90% attainment of equilibrium. This slow rate is probably not connected with the degree of crosslinking, since resin 1 had an equivalent rate. It may be due however to a concentration effect of the metal ion. Gregor et al.[49] have observed the decrease in capacity as metal ion concentration decreases, for various chelate ion exchangers. It is possible, therefore, as metal ion concentration decreases, so will the rate of diffusion across the interface of solution and resin i.e. film diffusion.

RESIN I

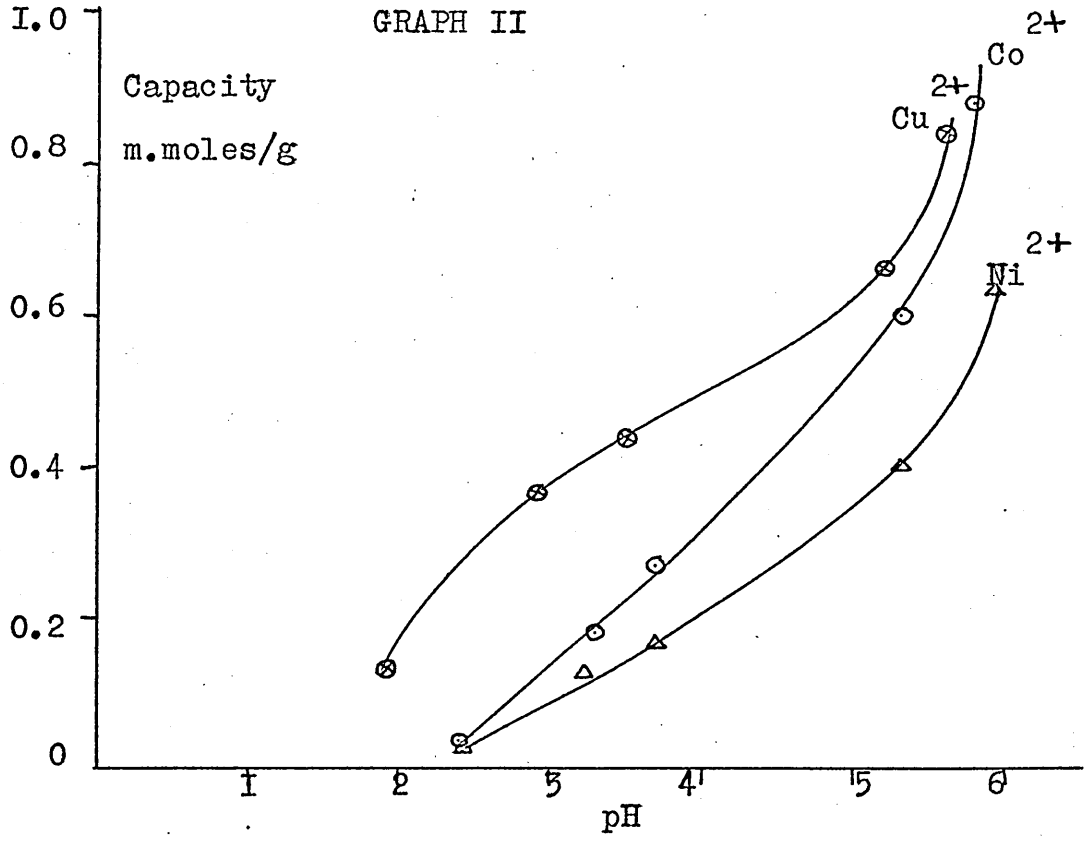
GRAPH 9

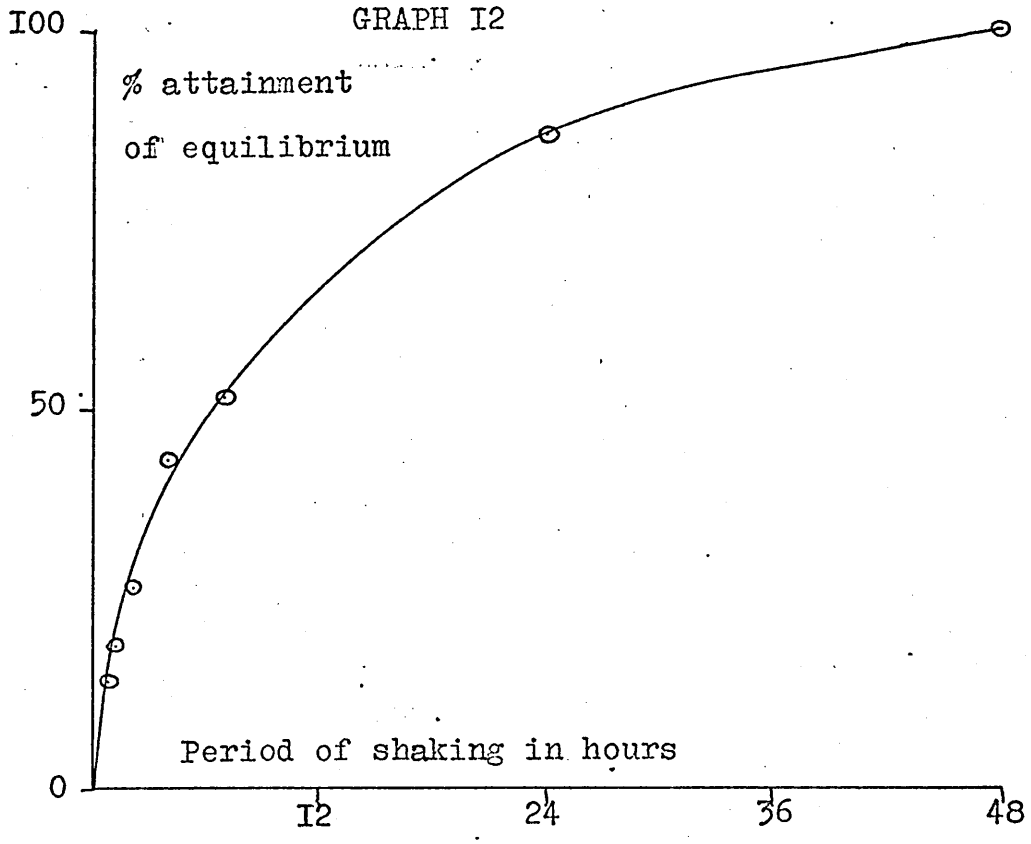


GRAPH IO



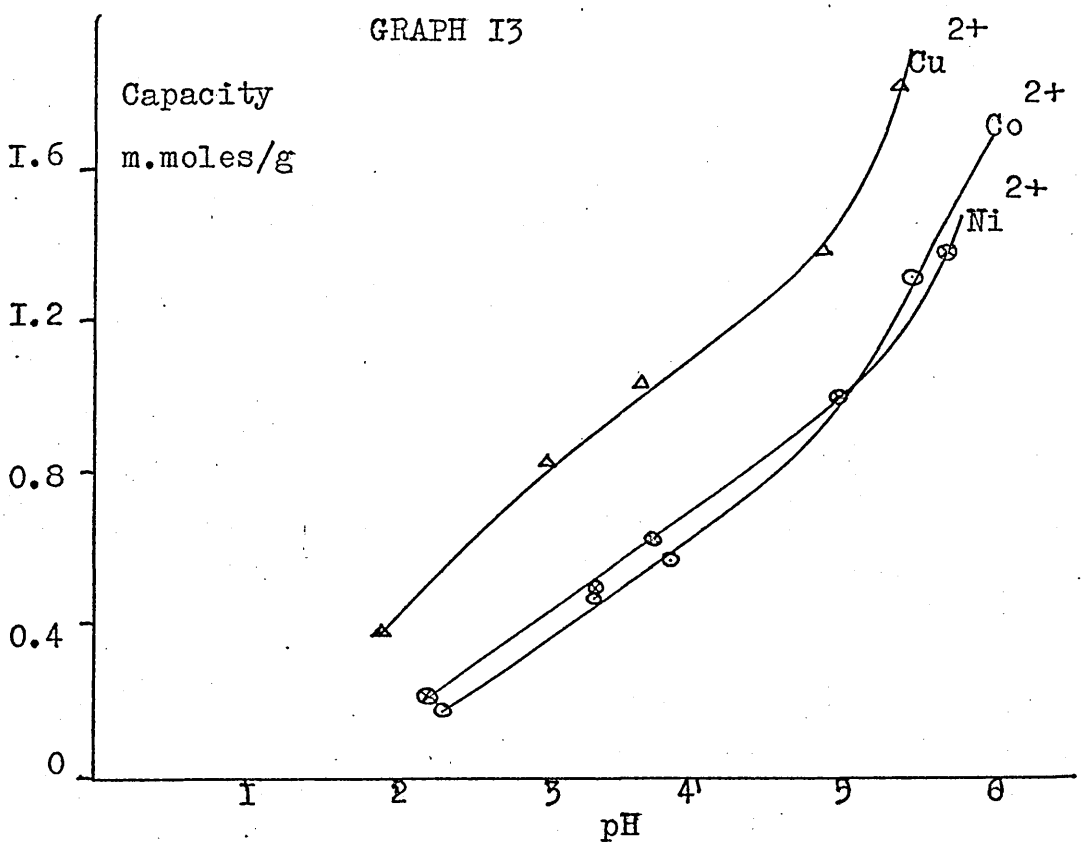
RESIN 2


GRAPH II
I.0
0.8
0.6
0.4
0.2
0
Capacity
m.moles/g
Co 2+
Cu 2+
Ni 2+
1
2
3
4
5
6
pH

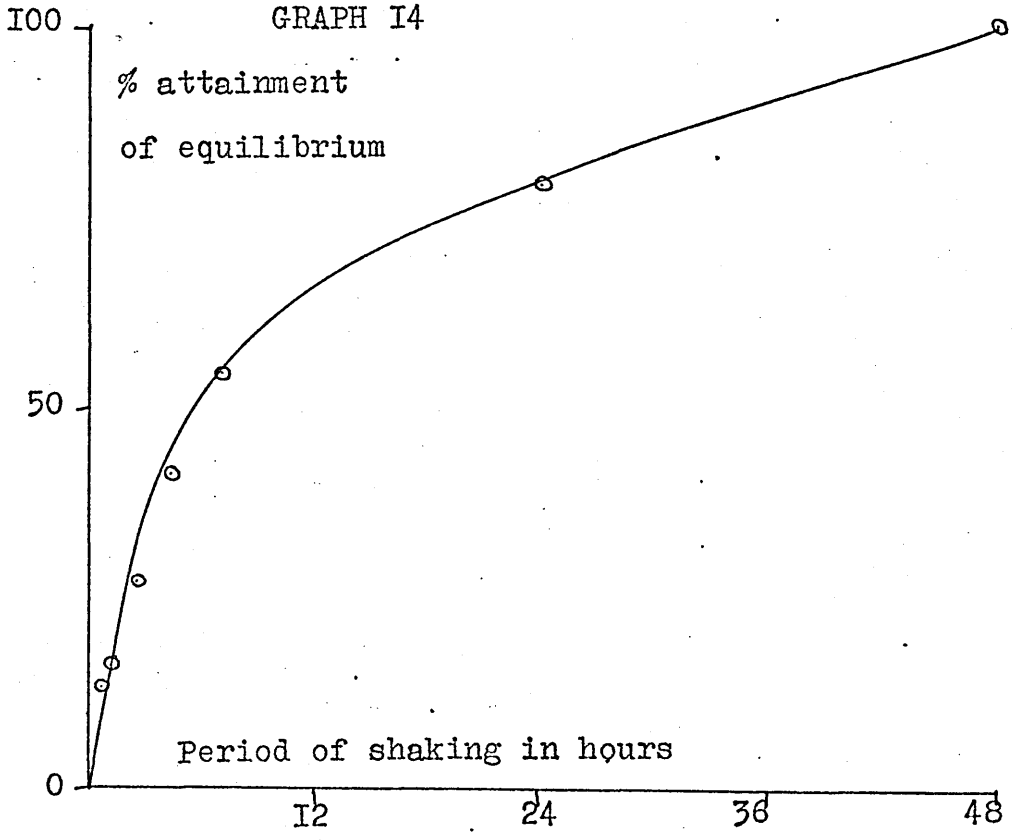

GRAPH I2
I00
50
0
% attainment
of equilibrium
Period of shaking in hours
I2
24
36
48

RESIN 3

GRAPH I3

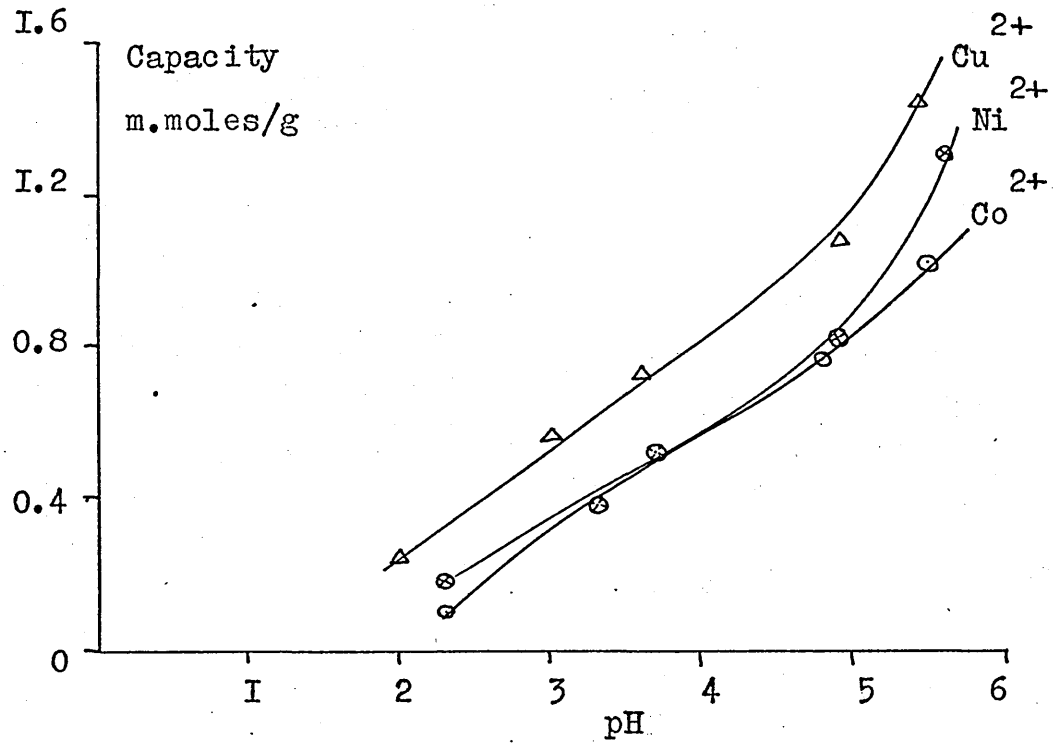


GRAPH I4

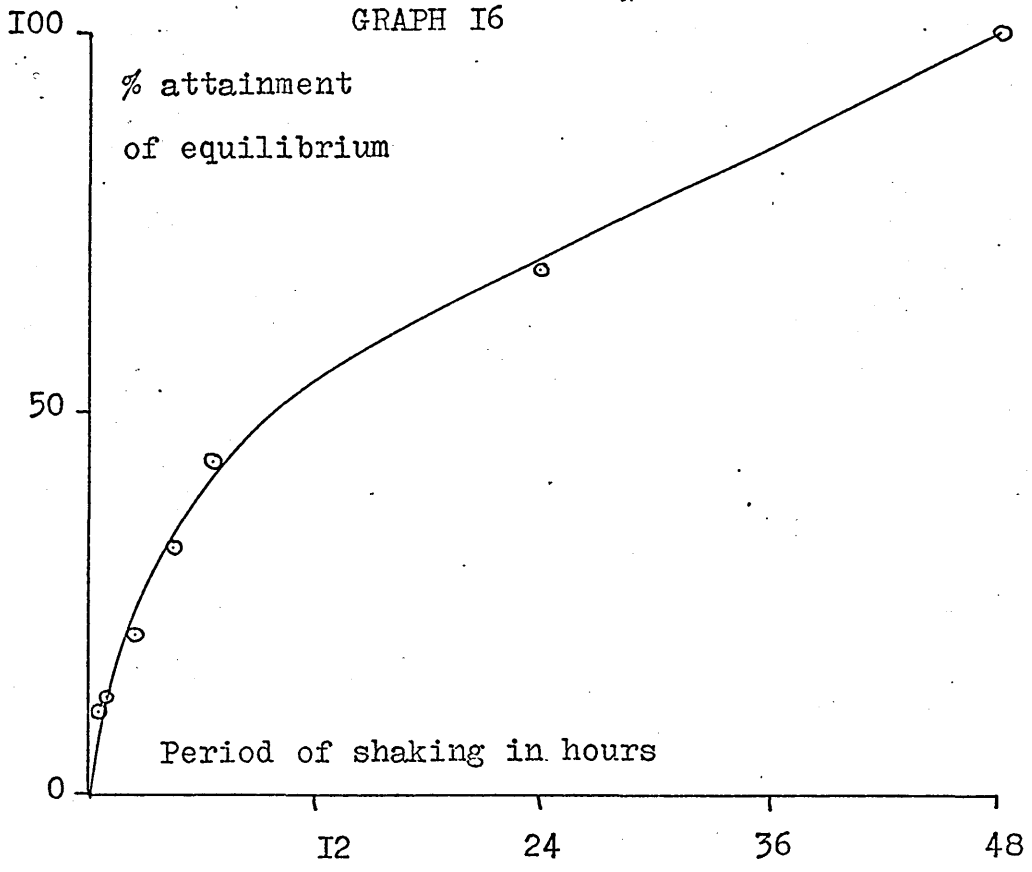


RESIN 4

GRAPH I5

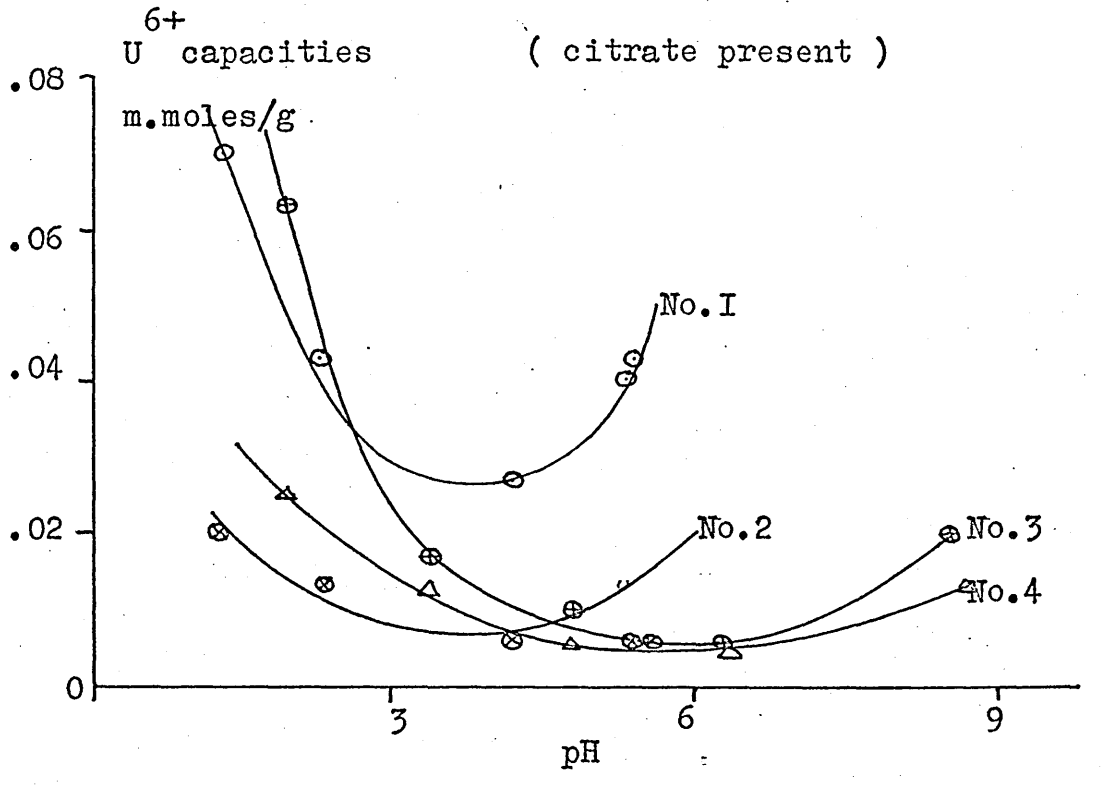


GRAPH I6

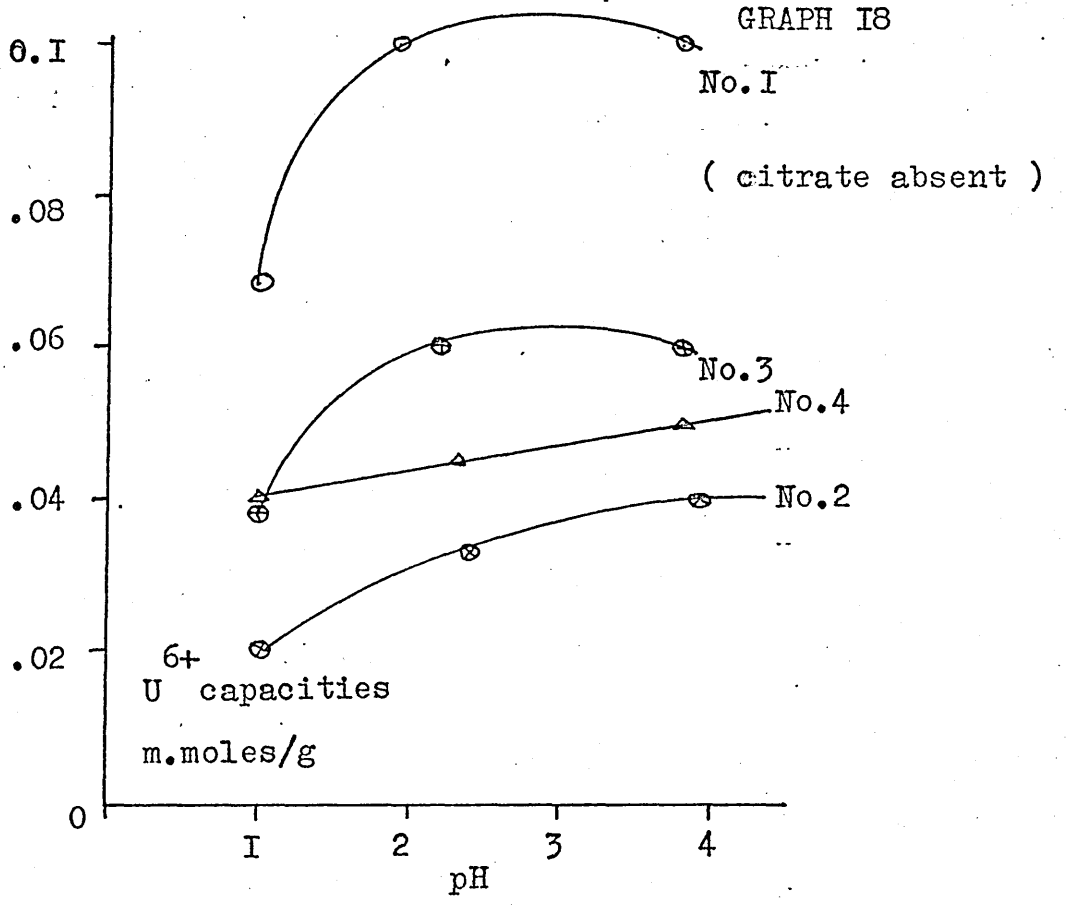


RESINS I,2,3 & 4

GRAPH I7



GRAPH I8



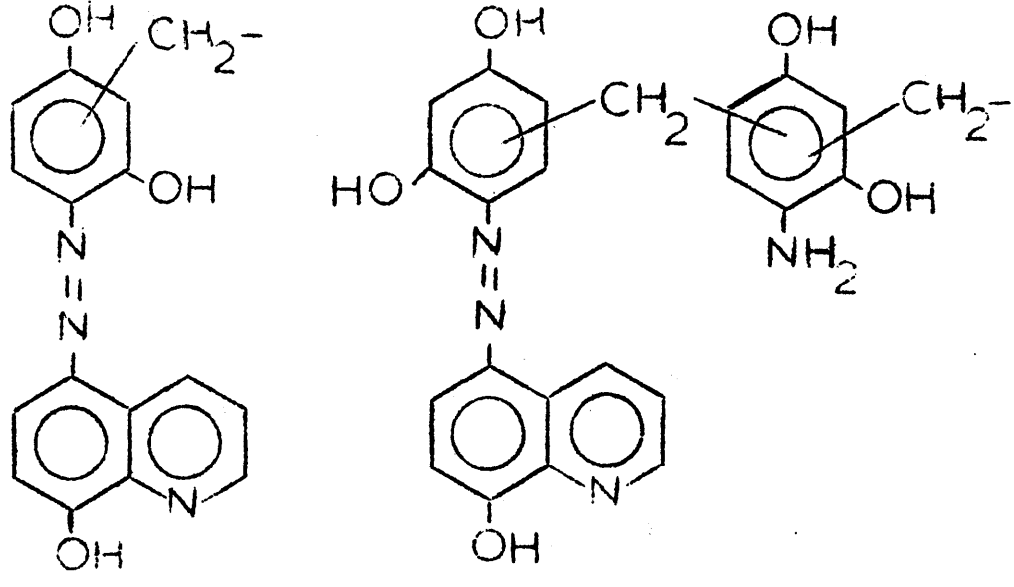
The stability of the resins were found to be good, no leaching out of chelating groups was observed for any of the four resins prepared. In order to solve the problem of which group present in the polymer was contributing most to the capacities, two 4-Nitroso-Resorcinol containing resins were prepared. No further modifications were carried out on these resins, so that the chelating site should be the nitroso and adjacent -OH group, unlike the previous four chelate ion exchangers where the "chelating" units could be:-

(1) Nitroso and adjacent -OH of the resorcinol.

(2) The oxine unit.

(3) The azo linkage and a -OH group of the resorcinol (figure A)

(4) The azo linkage and a NH_2 group of the resorcinol (figure B).



From the analysis of the resins, (Table 14) both concepts (3 and 4) are possible, since amino content of the resin is appreciable. It is possible however that with azo-amino coupling the distance between these groups (because of lattice intervention) may be too large for the smaller solvated metal ions, but might be favourable

for the larger ions i.e. possibly uranyl citrate species.

The two 4-nitroso-resins prepared had nitrogen contents comparable with those previously discussed. From Table 20 the number of m.moles of nitrogen or nitroso groups are 5.8 and 2.9/g. of resin respectively for the formaldehyde and formaldehyde-phenol copolymer. These resins for future reference will be referred to as 4-N.R.F. resin (4-nitroso-Resorcinol-formaldehyde) and 4-N.R.F.P. (4-nitroso-resorcinol-formaldehyde, phenol) copolymer.

Table 20

Resin	% element		
	C	H	N
4-N.R.F.	57.7	3.4	8.2
4-N.R.F.P.	64.9	4.3	4.0

The total theoretical capacities of the 4-N.R.F. and 4-N.R.F.P. resins are 5.8 and 2.9 m.moles of metal ion/g. of resin assuming a 1:1 complex is formed. The highest measured capacities for these resins were 2.30 and 0.32 for 4-N.R.F. and 4-N.R.F.P. respectively (Table 21). Their efficiencies are therefore 40% and 10% which is considerably less than the previous resins. This is partially true, but during the reduction step of the previous resins, nitrogen was lost. If an equivalent quantity of nitrogen in the resin is inactive as nitroso groups and isnot "chelating" with metal ions, due to modifications of the chelate site, then the efficiency of these resins would be 60 and 17% respectively.

Table 21

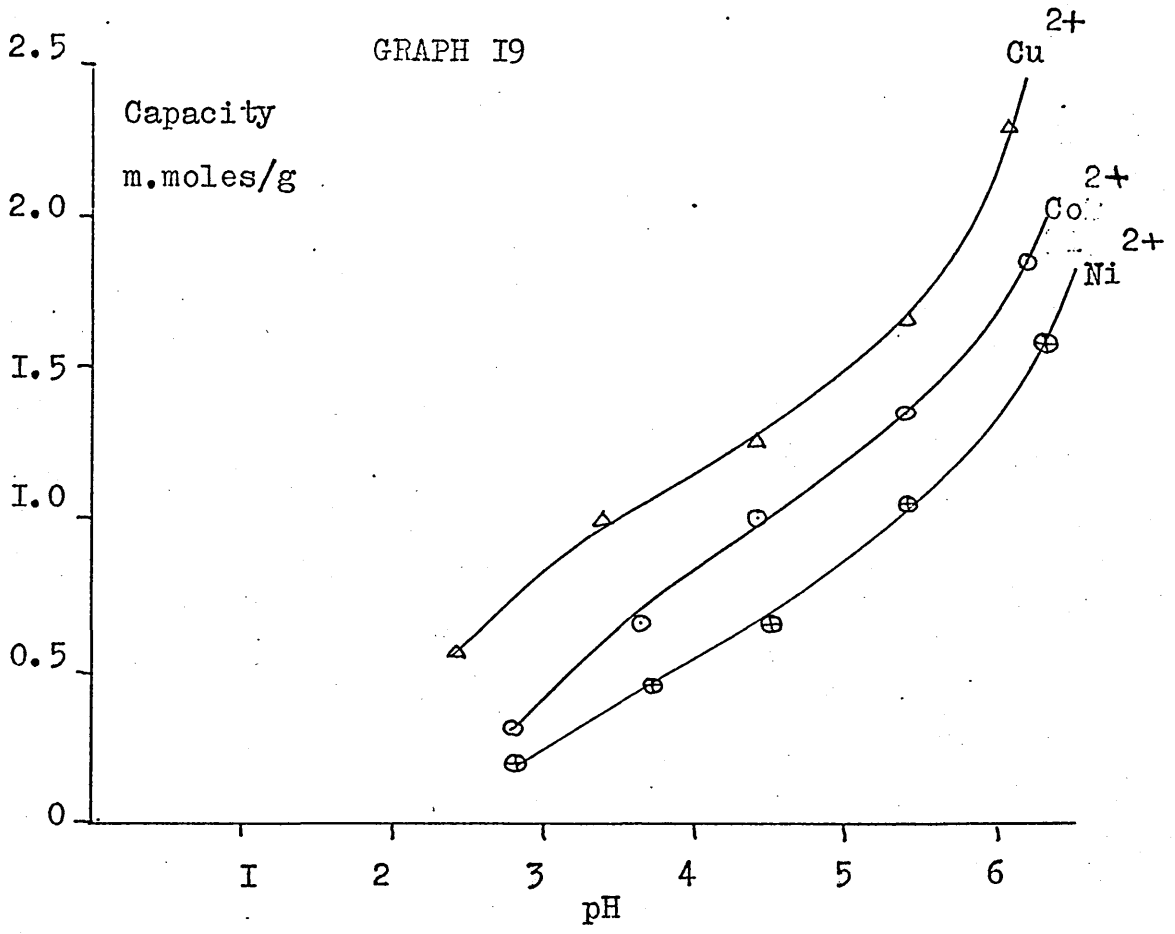
Resin	Metal ion	Capacity m.moles	Optimum pH
4-N.R.F.	Co^{2+}	1.87	6.2
	Ni^{2+}	1.57	6.3
	Cu^{2+}	2.30	6.0
	U^{6+}	0.04	1.6
4-N.R.F.P.	Co^{2+}	0.32	6.3
	Ni^{2+}	0.15	5.4
	Cu^{2+}	0.27	6.2
	U^{6+}	0.006	1.7-2.4

The capacities for 4-N.R.F. are superior to those of resin No.1 as would be expected from nitrogen content and higher pH values. The capacity is presumably lost in the previous resins due to the low yields of reduction and azo coupling. The order of capacities for the 4-N.R.F. resin is similar to that of resin No.1 i.e. $Cu^{2+} > Co^{2+} > Ni^{2+}$, but for uranyl ions in the presence of citrate is approximately half that of resin No.1. This may be due to the influence of the oxine units, in the latter case. When citrate is not present however the capacity decreases for 4-N.R.F. unlike resin No.1. This may be due to the increasing presence of HL^{3-} anions as pH increases, producing complex species of greater stability than nitroso resorcinol-uranyl systems.

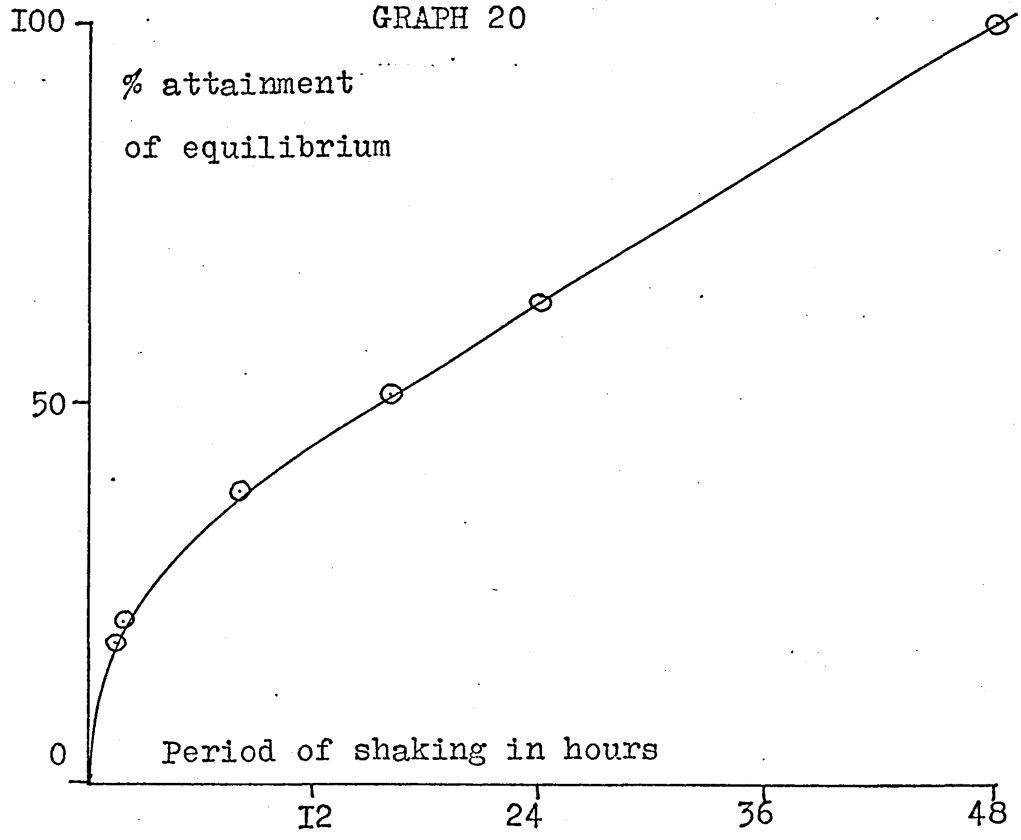
The capacities of 4-N.R.F.P. resins are lower than those of resin No.2, this should not be so. The major difference occurs with nickel, which exhibits a maximum capacity in the pH region 5.5 to 6.0 (graph 21). The low capacities may be due to a slightly more dense network compared with resin No.2, as the reduction step removes functional groups making the resin more porous. If the

4- N.R.F. RESIN.

GRAPH I9

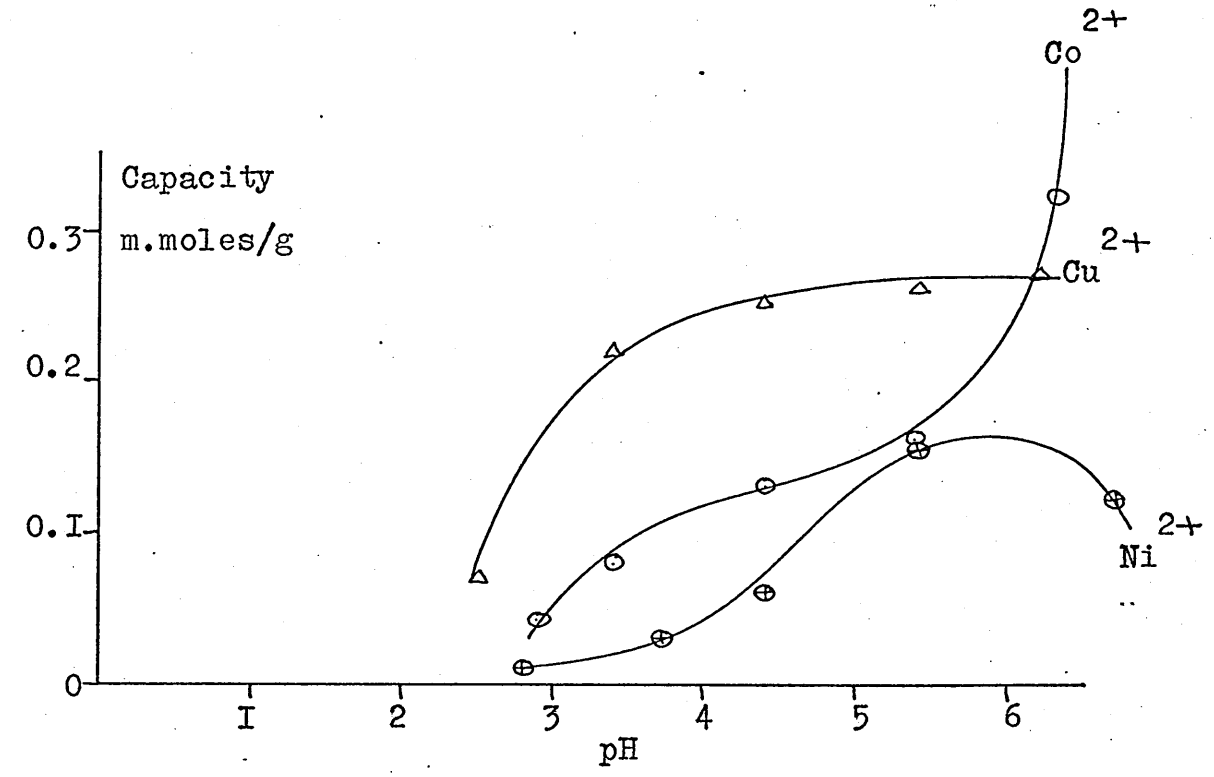


GRAPH 20

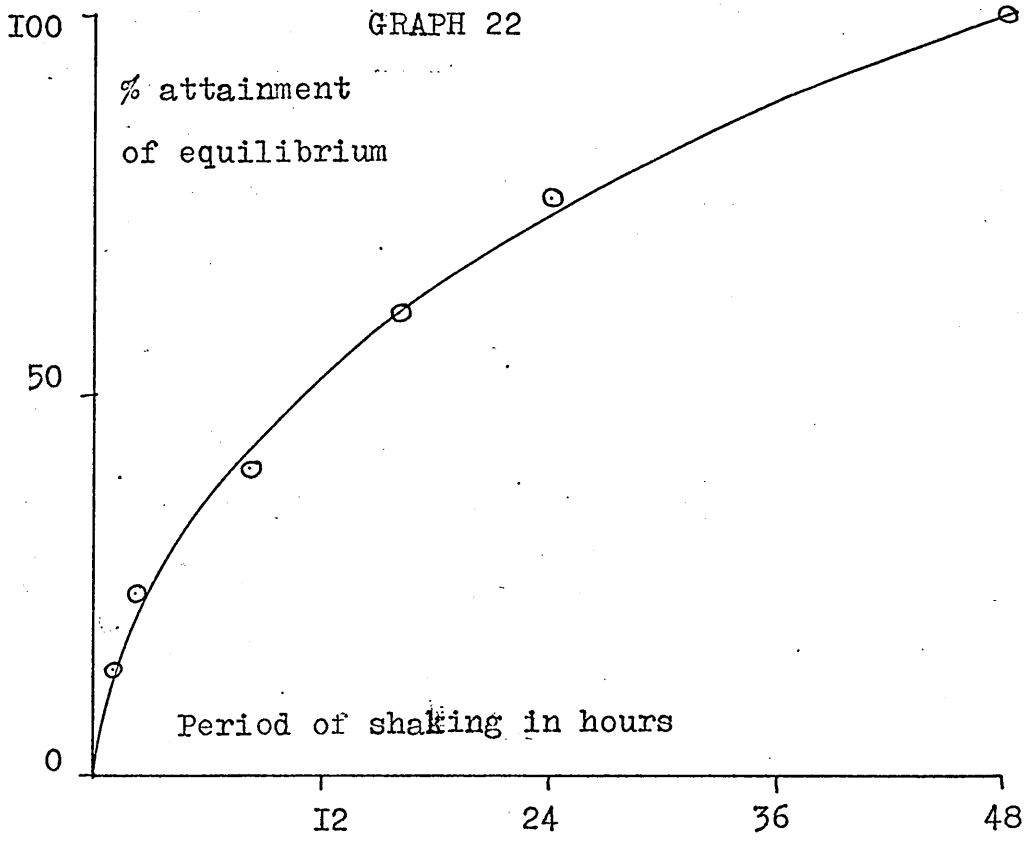


4- N.R.F.P. RESIN.

GRAPH 2I



GRAPH 22



matrix was slightly more dense then this would tend to favour nickel-having the smallest solvated radii. Apart from the oxine units present in resin No.2 contributing to this capacity effect, no other explanation can be offered. The uranyl capacities (graph 24) when citrate is absent would possibly suggest this as, for 4-N.R.F.P. resin they are constant over the pH region studied, but for resin No.2 an increase in capacity is observed as pH increases. The stabilities of both 4-N.R.F. and 4-N.R.F.P. resins were good, no leaching out of functional groups was found.

The rate of equilibration of copper (II) ions (graphs 20 and22) suggest that the resins are slightly more compact, since rates are slightly slower. The same argument however concerning slow rates of equilibration as used previously will apply to these two resins.

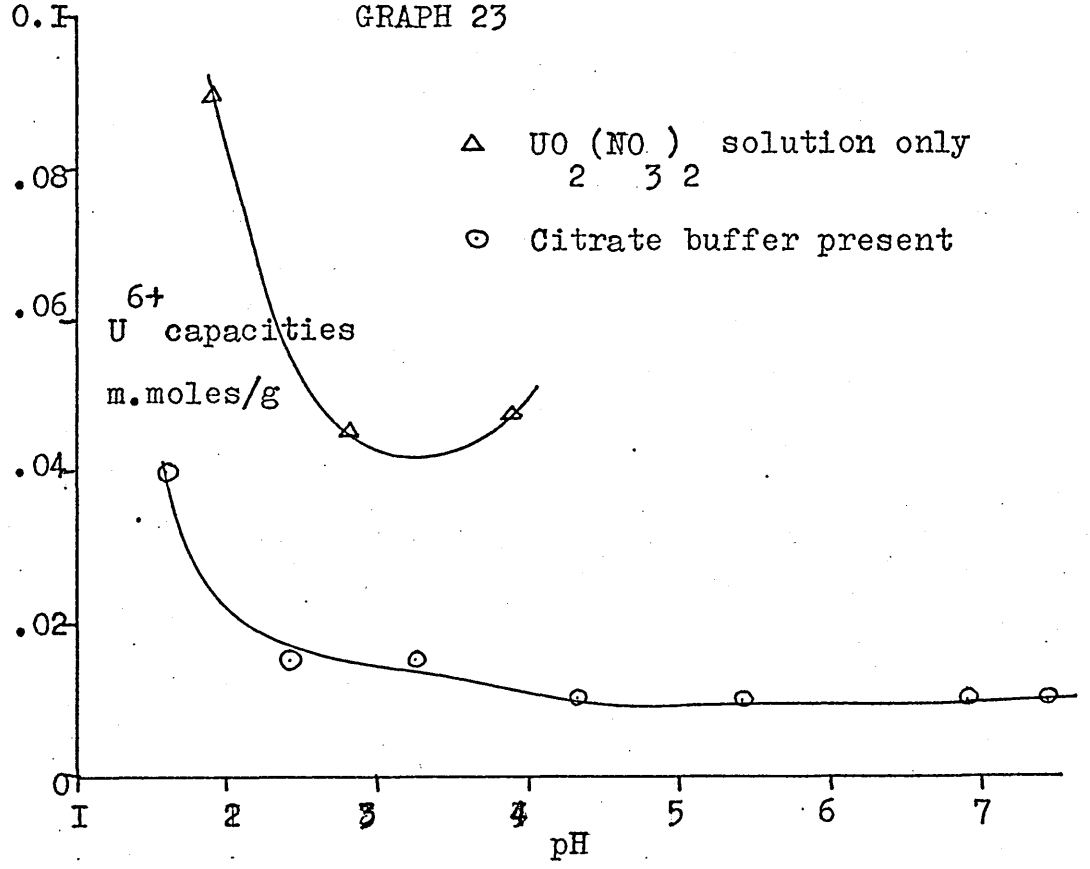
The reduction of the nitropolystyrene-divinyl benzene copolymer was only 59% efficient. This value is obtained from total nitrogen content of the nitropolymer (Table 22) and the amino content of the reduced form by non-aqueous titration. For simplicity these resins will be referred to as XAD2-.

Table 22

Resin	% element		
	C	H	N
XAD2-NO_2	60.6	4.6	8.9
XAD2-NH_2	66.2	6.0	9.1
XAD2-azo-oxine	69.6	5.6	7.7
XAD2-azo-P.A.R.	69.1	5.6	7.7
XAD2-azo-alizarin	67.5	5.4	6.2
XAD2-azo-salicylic acid	67.3	5.4	6.8
XAD2-azo-N,N^1 dimethyl aniline	68.5	5.6	7.9

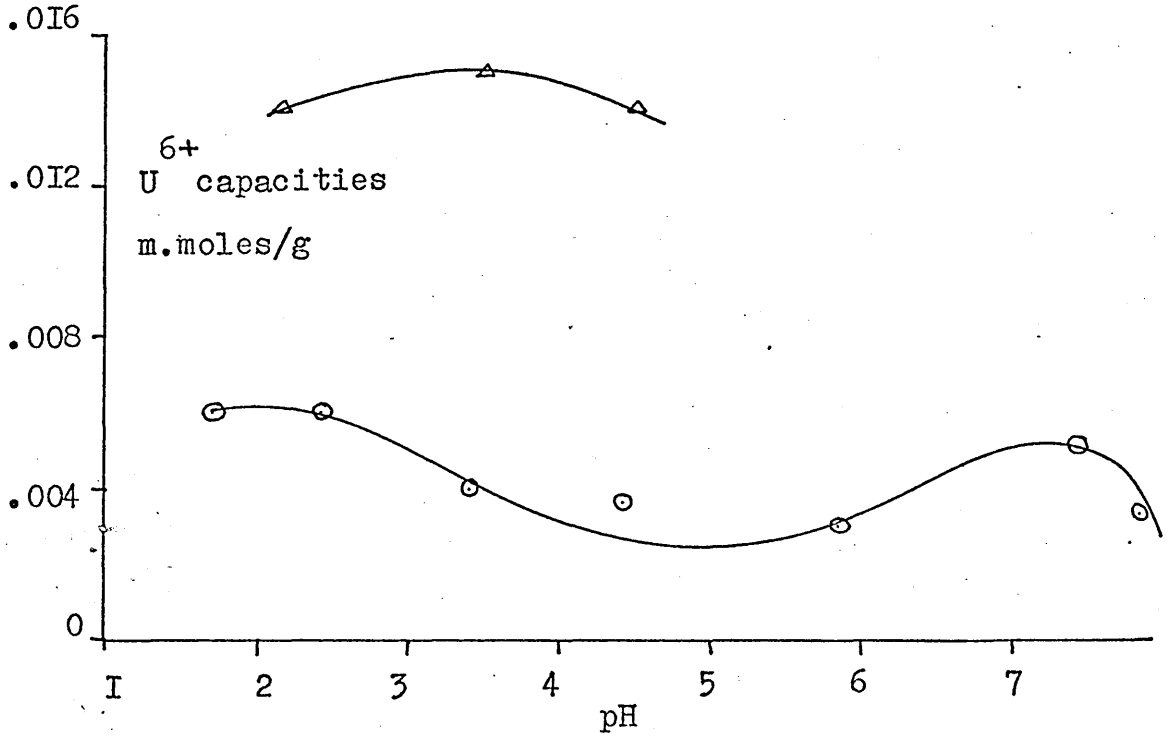
4- N.R.F. RESIN.

GRAPH 23



4- N.R.F.P. RESIN.

GRAPH 24



appropriate group i.e. XAD2-NO_2, XAD2-NH_2 etc.

Titrat able nitrogen content of the XAD2 NH_2 was 3.82/4.00 n.moles of nitrogen/g. of resin.

Using the previous mathematical technique an approximate idea of the composition per g. of resin can be deduced (Table 23).

Table 23

Resin	m.moles of nitro groups/g	m.moles of amino group/g	n.moles of chelating groups/g	% conversion of amino to azo linkage
XAD2 azo-oxine	2.65	0.71	0.72	76
XAD2 azo-P.A.R.	2.65	0.71	0.43	75
XAD2 azo-alizarin	2.65	0.94	0.40	46
XAD2 azo-salicylic acid	2.65	0.93	0.63	58
XAD2 azo-N,N' dimethyl aniline	2.65	0.63	0.79	78

If this treatment is corret, the XAD2 azo, -oxine, -P.A.R., -alizarin and -salicylic acid resins should have total capacities for multivalent metal ions of 0.72, 0.43, 0.40 and 0.63 m.moles/g. respectively. This is easily checked for the XAD2 azo-salicylic acid resin by titrating either the total number of replaceable hydrogens (using sodium hydroxide) or the carboxylic acid protons only (using sodium carbonate solution). The titratable proton values were 1.34 m.moles/g. (total) and 0.70 for carboxylic acid protons. These values are generally in good agreement with the calculated values. The measured capacities however are higher than the calculated values (Tables 24, 25, 26 and 27), it was first proposed that the remaining nitro groups within the resin matrix could be forming a chelate. This has been suggested for

nitrophenol-type ion exchangers prepared by Saito[109] et al. and also for p-nitrophenol in general[107]. The measured cobalt capacity of the polynitro styrene-divinyl benzene copolymer was <0.05 m.moles/g. This was to be expected however on reviewing the possible chelating sites available, i.e. only nitro. The second proposal was that the poly amino styrene-divinyl benzene could have a capacity for metal ions, either by direct donation of lone pair of electrons, as with pyridinium complexes, or that both nitro and amino groups were "co-ordinating" the metal ions. This proposal was also invalid as the resin had little or no affinity for metal ions. It must be assumed, therefore that this "extra" affinity for metal ions by these four resins, is due to interactions between say amino groups (actually the lone pair of electrons) and the azo linkage. If this is true, then the combined capacities (theoretical) of these resins are within the range 1.2 to 1.6 m.moles/g. (Table 23). In order to verify this possibility of the azo linkage co-ordinating metal ions, a resin containing N,N^1-dimethyl aniline was prepared. Azo coupling of XAD2 diazonium salt to N,N^1 dimethyl aniline was carried out in an acetate medium (pH 5.6).

Table 24 XAD2 azo-oxine resin

Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	0.25	5.9
Ni^{2+}	0.10	6.2
Zn^{2+}	0.33	6.2
Cu^{2+}	0.48	5.5
Al^{3+}	0.26	4.3
U^{6+}	0.11	2.0

Table 25 XAD2 azo-P.A.R. resin

Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	0.29	5.8
Ni^{2+}	0.23	6.1
Zn^{2+}	0.33	6.1
Cu^{2+}	0.72	5.4
Al^{3+}	0.27	4.3
U^{6+}	0.126	2.3

Table 26 XAD2 azo-alizarin

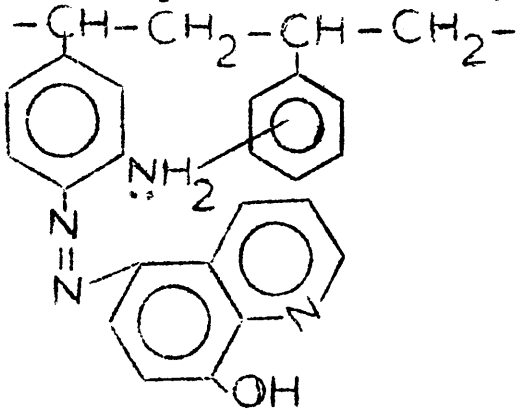
Metal ion	Capacity m.moles	Optimum pH
Co^{2+}	0.26	5.8
Ni^{2+}	0.29	6.1
Zn^{2+}	0.30	6.6
Cu^{2+}	0.69	5.4
Al^{3+}	0.29	4.4
U^{6+}	0.09	3.0-4.2

Table 27 XAD2 azo-salicylic acid

Metal ion	Capacity m.moles	Optimun pH
Co^{2+}	0.19	5.6
Ni^{2+}	0.34	5.5
Zn^{2+}	0.25	5.6
Cu^{2+}	0.93	5.2
Al^{3+}	0.71	4.7
U^{6+}	0.14	3.0-4.0

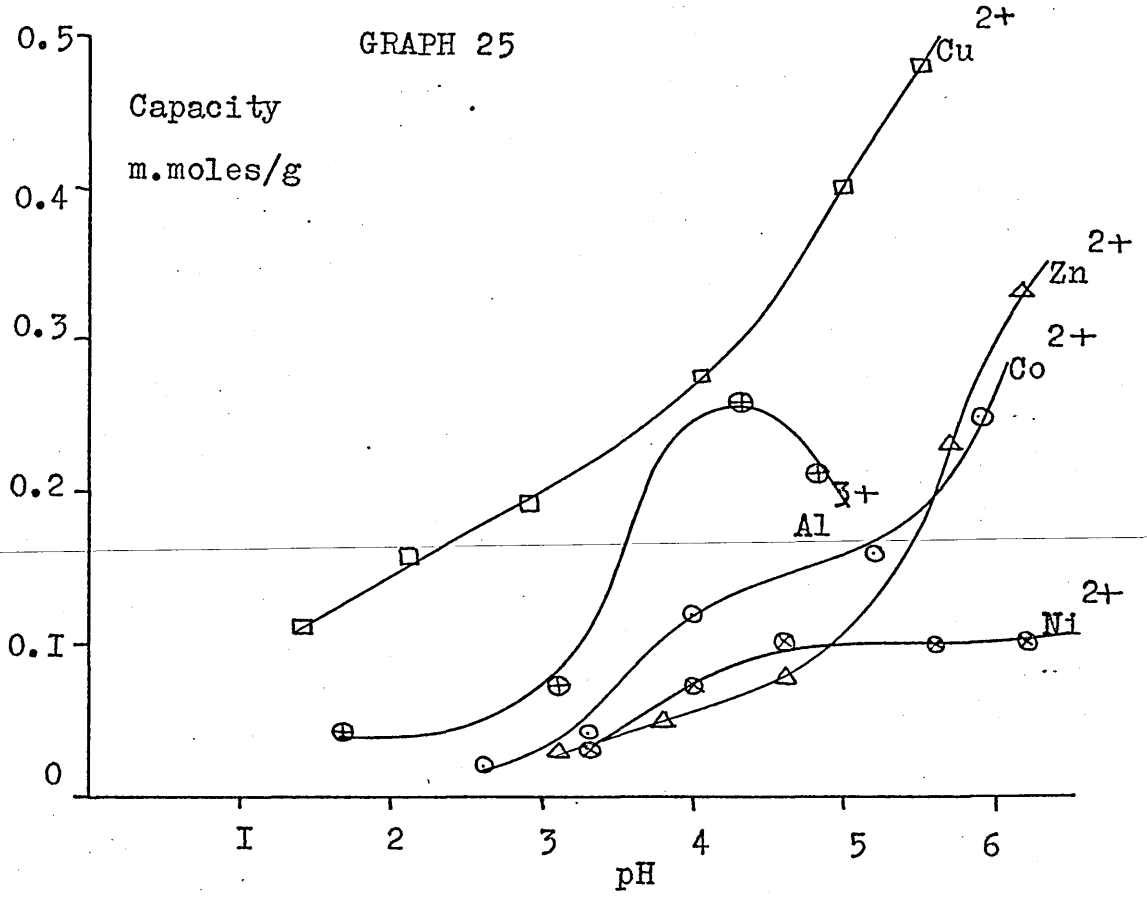
The capacities for Copper (II) and cobalt (II) ions were 0.60 and 0.12 m.moles/g. respectively for the XAD2 azo-N,N[1] dimethyl aniline resin. The capacity for metal ions from theoretical aspects is 0.79 m.moles/g. of resin (Tabel 23). It is highly unlikely that chelation occurred via lone pair donation of the nitrogen atom to the metal ion, or that this resin behaved as an anion resin, since these capacities were determined at a pH of 5.6. There are sufficient amino units remaining i.e. 0.63 m.moles to suggest chelation occurred via the azo linkage and lone pair donation of electrons from the amino unit.

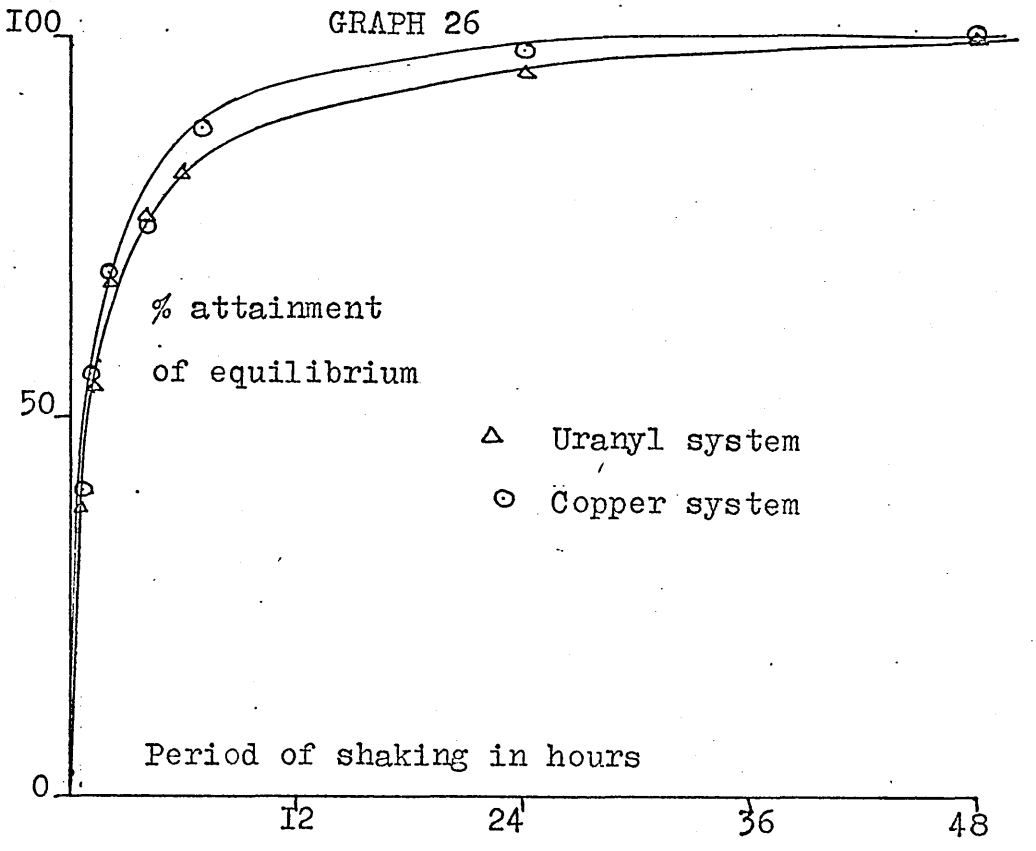
From the measured capacities of the XAD2 azo-oxine resin, and the theoretical capacity, it is unlikely that the azo linkage is participating in bond formation. Generally coupling of oxine to a diazonium compound occurs in the 5-position.



It is unlikely therefore that the oxine functional units could influence any bond formation between an azo linkage and metal ion. It is possible however that if this bonding had occurred the influence of an adjacent amino unit could stabilise such bond formation, through lone pair donation. The order of stability for divalent metal ions with oxine is Cu > Ni > Co > Zn[16]. If the capacity of the metal ions can be qualitatively regarded as being a function of stability of the metal complex formed, then the above series is partially correct. Any major differences in capacities cannot be equated to the size of the hydrated metal ion being too large to enter the resin matrix. Since coupling of the oxine molecule to the resin matrix is far removed from the chelating sites of oxine, it is unlikely that modifications to these has occurred. Therefore the idea of hydrated metal ions being too small will also be invalid. The criterion could be at which pH the capacities are related to the stabilities of metal oxinates. As the pH increases beyond 4.0, the stability of the Al-complex with the resin becomes less favourable. If the capacities of the resin are taken at pH 4.0 (graph 25), then the order of capacity is $Cu^{2+} > Al^{3+} > Co^{2+} > Ni^{2+} > Zn^{2+}$, with the exception of Co^{2+}, this series is similar to the one previously quoted. However, during "chelation" of the metal ion to the resin, a 1:1 complex is being formed, it is necessary therefore to consider only the first stepwise formation constant (K_1). These are 12.56, 10.55 and 9.9 for Cu^{2+}, Co^{2+} and Ni^{2+} respectively for the oxinates[110]. The capacity of XAD2 azo-oxine for uranyl ions is low (Graph 33) when citrate buffer is present. The maximum capacity occurs within the pH region 0.9 to 1.8, and shows a steady decrease from 1.8 to 6.0, becoming relatively constant

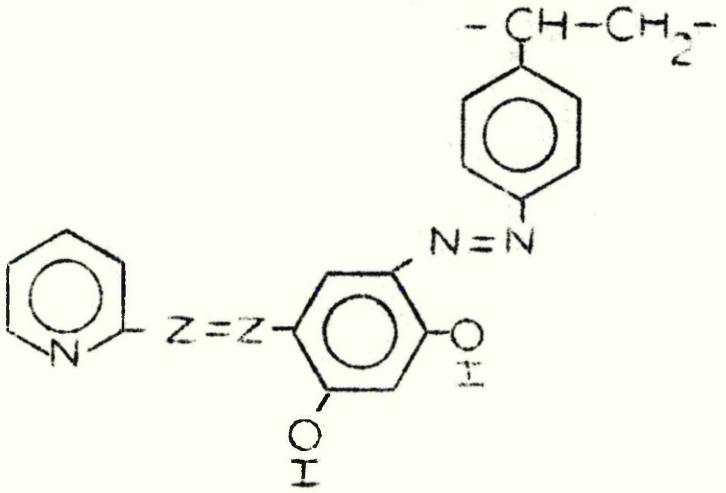
XAD2 azo-OXINE.



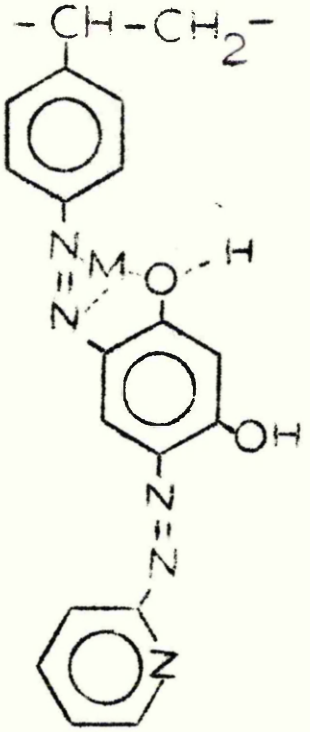


at 6.0 to 9.5. The low capacity will be due to the citrate ions in solution being in competition for uranyl ions with the oxine units. The equilibrium lies in favour of the uranyl citrate complex, as concentration of citrate is greater than the concentration of oxine molecules available. From solvent-extraction of the oxine-uranyl system it may have been proposed that the resin should have increased its capacity for uranyl ions as pH increased i.e. $0 \rightarrow 9$. The nature of the complexes formed between the resin and oxine itself are totally different. With solvent extraction, a UO_2OX_2HOX species is formed, which is unlikely to be formed with the oxine units coupled to the resin. It is possible therefore, that the complexes formed between citrate and uranyl ions are the predominant factor, above pH 2.0.

From the measured capacities of the XAD2 azo-P.A.R. resin, it has a higher affinity for Copper (II) ions than any other XAD2 resin with the exception of salicylic acid. This copper affinity however in approximately twice that of the theoretical capacity of the P.A.R. units. In order to explain this, the coupling of P.A.R. to the styrene matrix may have possibly occurred in the 6 position, i.e.



It is possible therefore that the copper ion could form a tridentate complex with the two nitrogens and the oxygen of resorcinol.

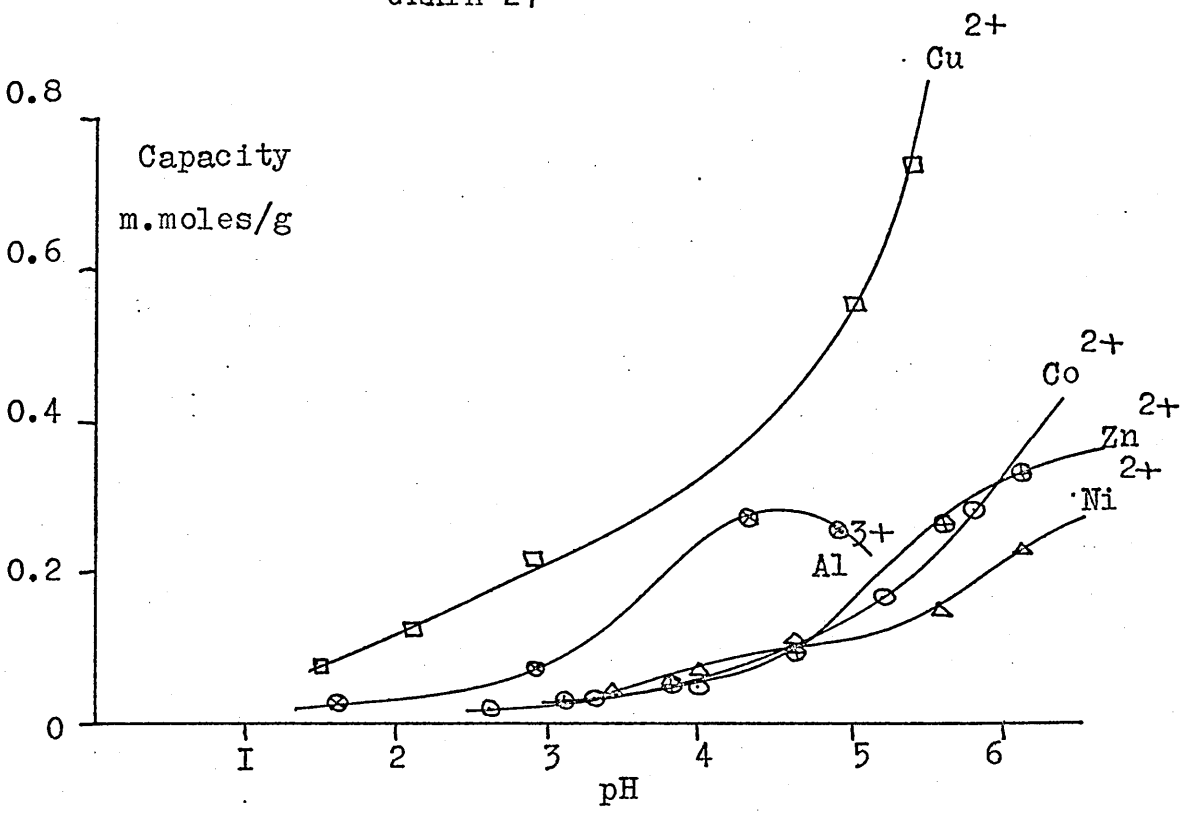


The possibility of azo co-ordination is valid since the capacity of the XAD2 azo-dimethyl aniline resin was higher for copper (II) ions than for cobalt. The co-ordination properties of benzene azo-resorcinol have been reported previously[86,117]. Greary et al.[86] compared the copper complexes of P.A.R. with those of benzene azo-resorcinol, the major difference, apart from stabilities, was the insolubility of the latter complex in water. Unfortunately no specific data have been reported concerning the stabilities of these complexes, although every indication is that the copper (II) ion readily forms complexes. Kaneniwa[117] investigated azo phenols, which formed stable complexes with Cu, Co and Ni(II) ions in 0.5N sodium hydroxide solution, but Zn, Cd and Mn(II) ions did not form complexes.

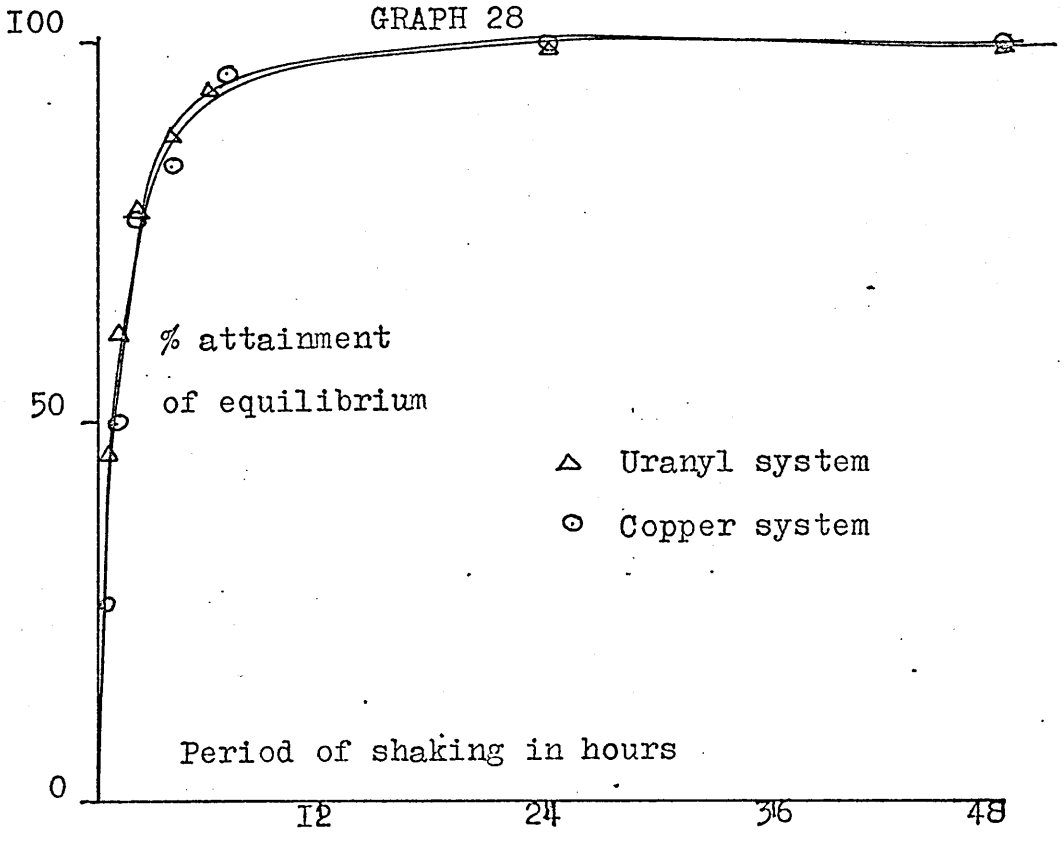
The remaining measured capacities are of the same order as the calculated values and it will be assumed therefore that the

XAD2 azo-P.A.R.

GRAPH 27

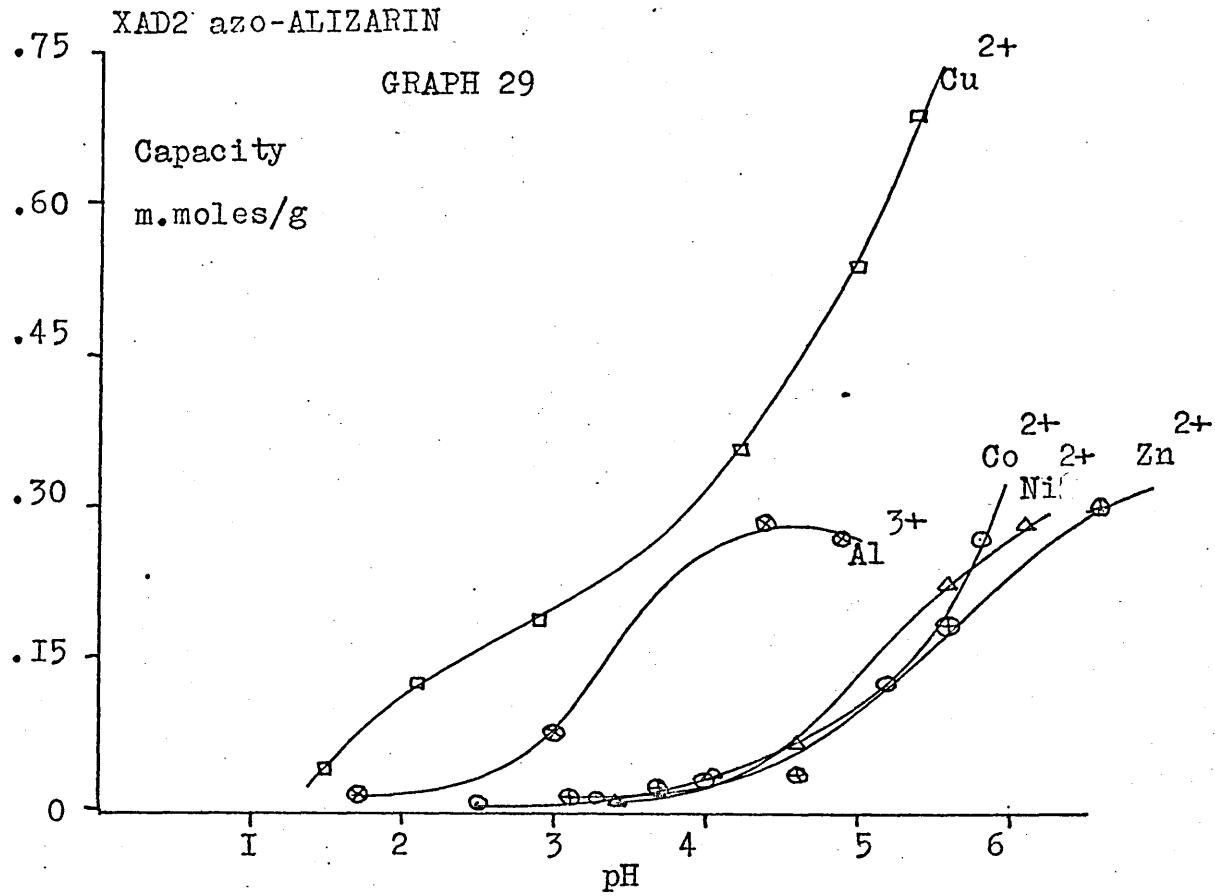


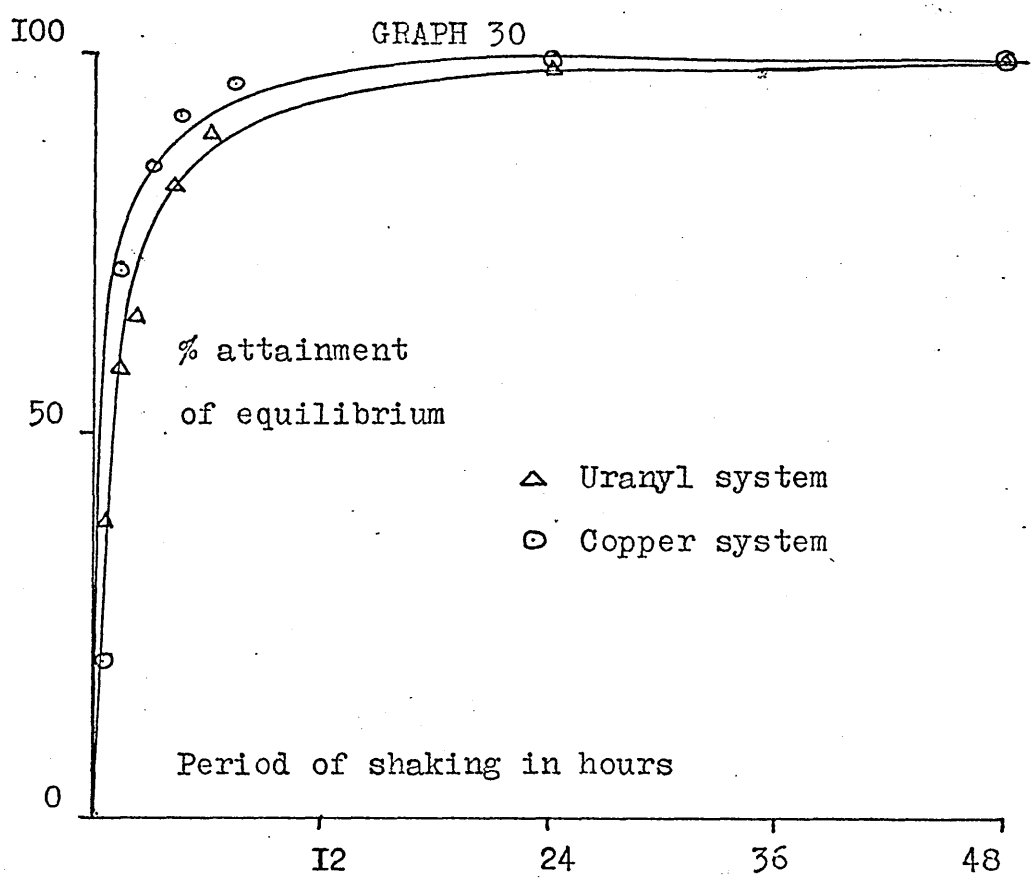
GRAPH 28

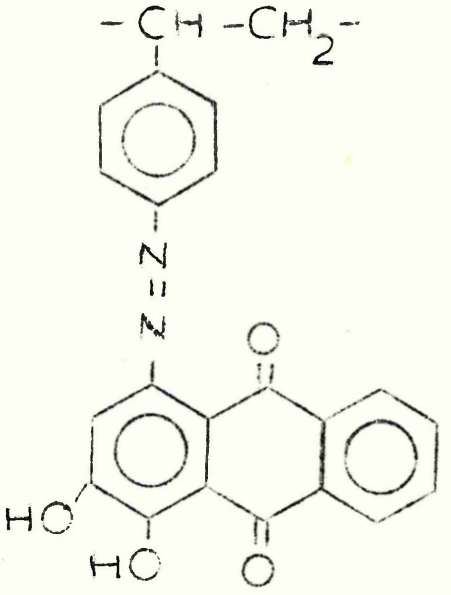


P.A.R. ligand is the functional unit. Unlike the oxine resin, the nickel capacity did not reach a maximum at pH 5, but similarity is apparent in their behaviour towards Al^{3+} and U^{6+}. The order of stability of P.A.R. complexes is $Cu^{2+} > UO_2^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+}$, and from the measured capacities would suggest the order to be (at pH 4.0) $Cu^{2+} > Al^{3+}$ with Co^{2+} Ni^{2+} and Zn^{2+} having approximately the same stability (Graph 27) but less than Al^{3+}. The orders are relatively similar to the stabilities of Co^{2+}, Ni^{2+} and Zn^{2+} P.A.R. complexes which are 14.8, 13.2 and 12.4[86,87] respectively. The problem is however why UO_2^{2+} ions should have a low capacity when the P.A.R.-UO_2 complex has a stability of 16.2[86]. This low capacity will be due to the presence of citrate ions, it is however higher than that of the oxine resin, which might suggest that the oxine-uranyl complex is weaker than P.A.R. uranyl complex, and in fact this is generally true. As the pH increases the equilibrium associated with the P.A.R. uranyl complex possibly decreases giving lower capacities or alternatively may be due to the citrate medium.

A similar type of stability order exists for XAD2 azo-alizarin, as did with P.A.R. The highest measured capacity being that for copper which is too great to explain in terms of alizarin "chelation" alone (Table 26). The measured capacity is approximately 75% greater than the theoretical, and can only be explained in terms of azo participation. The mode of coupling of alizarin to the polystyrene back bone will presumably be influenced by -OH groups present and will occur at the 4 position thus:


XAD2 azo-ALIZARIN
GRAPH 29
Capacity
m.moles/g
.75
.60
.45
.30
.I5
0
Cu 2+
Co 2+
Ni 2+
Zn 2+
Al 3+
I
2
3
4
5
6
pH


GRAPH 30
I00
50
0
% attainment
of equilibrium
Uranyl system
Copper system
Period of shaking in hours
I2
24
36
48

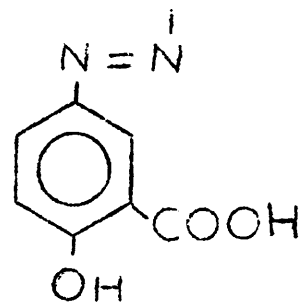


It may be possible that the carbonyl oxygen will influence bond formation with a metal ion greater than an adjacent amino unit. From the measured capacities the order of stability could be regarded as being Cu^{2+} > Al^{3+} > Co^{2+}, Ni^{2+} and Zn^{2+} at pH 4.2 (Graph 29). This order is possibly correct, but as no values have been reported for alizarin complexes no comparative comments can be made. The uranyl capacities bear a distinct resemblance to the XAD2 azo-salicylic acid system (Graphs 33 and 34). Both show a maximum within the pH range 3.0 to 4.2, and a steady decrease as pH drops. There is in each case a slight increase in the capacities at pH's above 9.0. This may be due to a different uranyl citrate species being formed which has a lower stability, this is unlikely however as the XAD2 azo-PAR resin would have also shown a possible increase. Alternatively it may be due to an exchange process of NH_4^+ ions for the hydroxy hydrogens of both alizarin and salicylic acid, which in turn is an equilibrium exchange of uranyl ions for NH_4^+ ions.

The XAD2 azo-salicylic acid bears little resemblance to the condensation resin, the solvated metal ion size is comparatively unimportant with polystyrene resins. The condensation salicylic acid polymer should have had capacities greater than the XAD2. This role is reversed and the copper measured capacity of XAD2 azo-salicylic acid is greater than the sodium-hydrogen exchange value. The Al(III) capacity of the condensation resin is at a maximum within the pH range 4.5 to 5.0 (Graph 5). Whereas the XAD2 resin does reach a maximum below pH 4.7. The resins show some similarity in the positioning of metal ions in a stability order i.e. with the XAD2 resin $Al^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$, taken at pH 4.5 (Graph 31). This order is identical with the orders of stability for salicylic acid metal complexes.

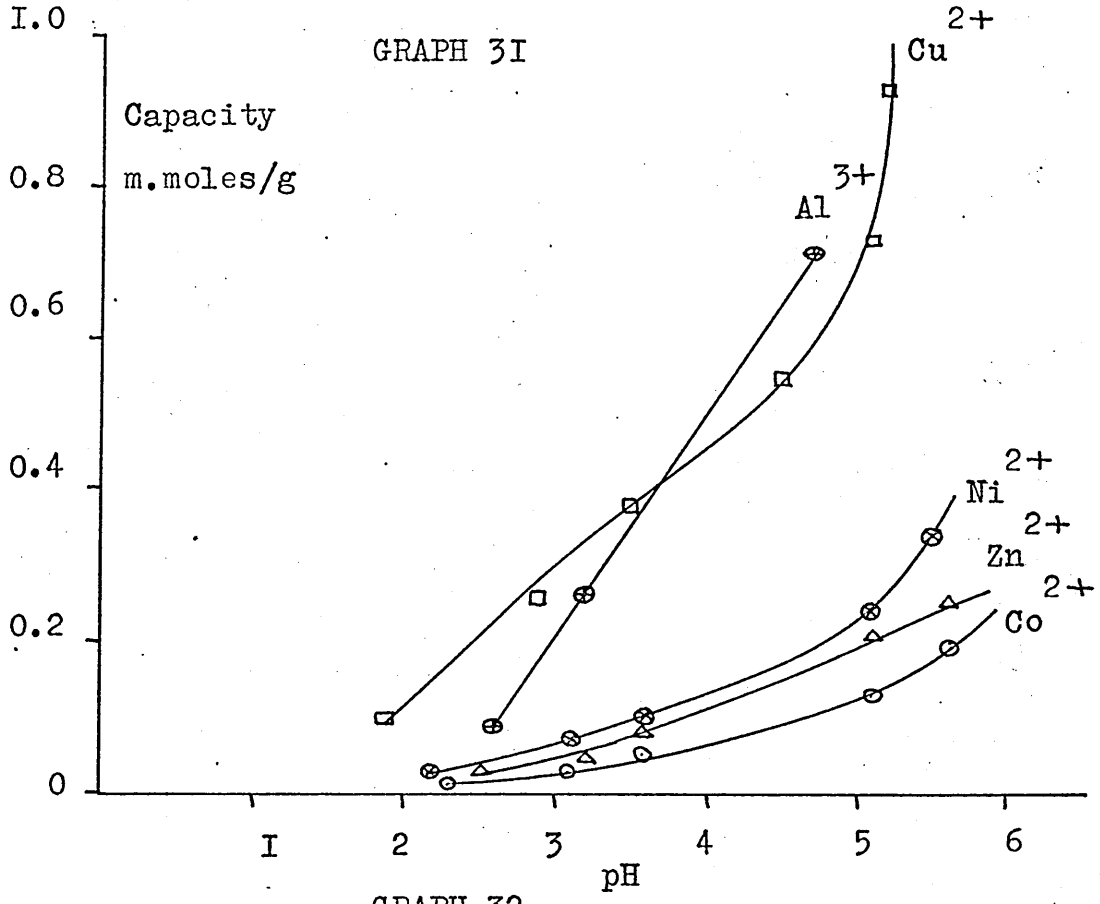
The capacity for uranyl ions for the condensation salicylate resin shows a maximum at higher pH values whereas the XAD2 resin has a maximum within the pH range 3.0 to 4.0.

The maximum uranyl capacity occurring at pH 7.7 for the condensation resin, could be due to the resin matrix swelling in alkaline solutions. This may be true also for the XAD2 resin but is unlikely as the uranyl ions have ready access to the chelating sites over the whole pH range studied. This difference could be a result of the resin matrix itself, i.e. with XAD2 salicylic acid resin, azo coupling will occur in the 4 position thus.

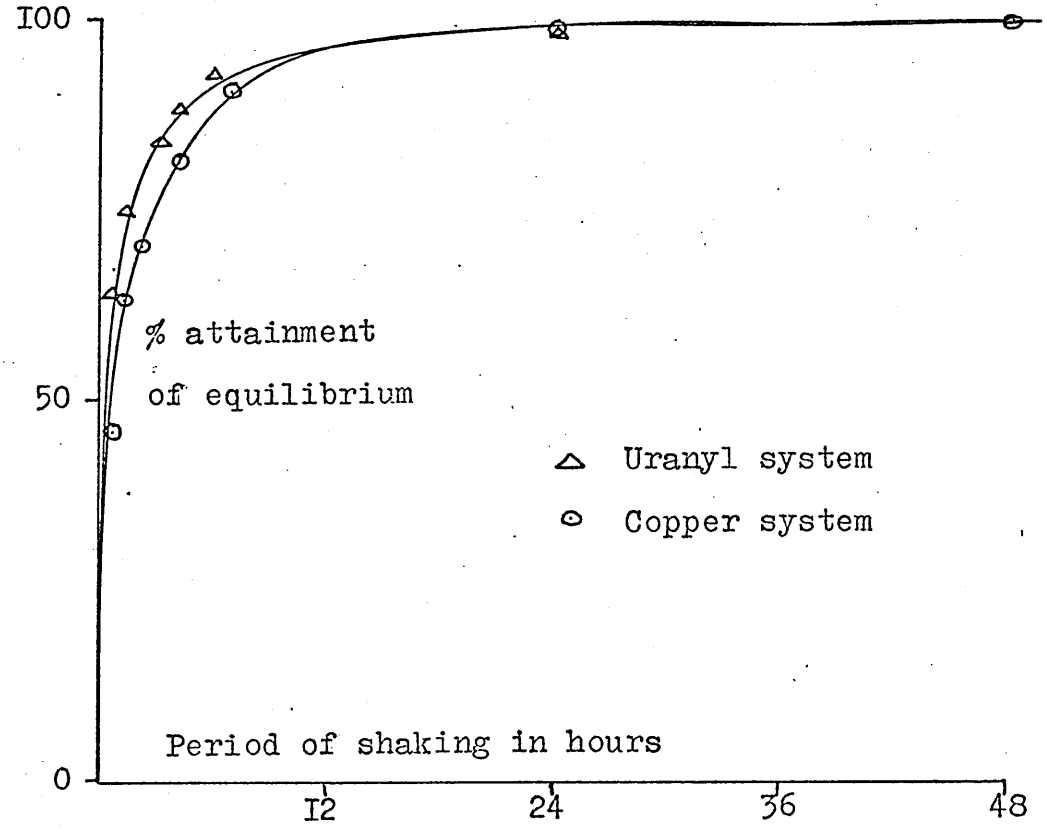


XAD2 azo-SALICYLIC ACID

GRAPH 31



GRAPH 32



It is possible therefore that any "extra" capacity will have to be achieved via the azo bond and the lone pair on adjacent amino groups. This applies for Cu^{2+}, but for Al^{3+} may be doubtful. The aluminium capacity is only 12% above the theoretical value, which itself is only an approximation to say within approximately $\pm$ 10%.

With all of these XAD2 resins the highest measured capacities were for copper. How much the azo unit itself contributed towards this is debatable. The predominant effect will be the relative magnitudes of the stability constants for the resin complex and azo complex when a competing chelate is present. Some indication of this might be evident in a later section regarding stability measurements of metal ion chelate resin systems. The stability of all the XAD2 resins were good, no leaching out of functional units was evident on recyclisation of the samples. The resins were generally stored in sealed bottles, and were air dired, (having moisture content 2-5%), no detrimental effects were observed in keeping the resins in this condition. The validity of the procedure for measurement of capacities can be observed from Table 28. The initial capacity refers to the technique adopted by other workers in this field[38,49], namely measurement of metal ion concentration before and after equilibration. The final capacity refers to the technique used in this investigation.

Table 28

pH	Initial capacity	Final capacity	Resin
2.8	0.033	0.036	XAD2
3.6	0.047	0.042	azo-P.A.R.
4.2	0.062	0.058	
5.2	0.128	0.126	
5.7	0.171	0.168	
			XAD2
2.8	0.135	0.132	azo -
3.6	0.078	0.073	Alizarin
4.2	0.030	0.028	
5.2	0.021	0.022	
5.6	0.018	0.019	

The values in columns 2 and 3 are expressed in m.moles/g. of resin. The metal ion was cobalt (0.004m) in acetate buffers.

The rates of equilibration of the four XAD2 resins were measured for both copper (II) and uranyl (II) ions. With the latter no buffer was used, whereas acetate buffer was used for the copper system. All four resins had equilibration times of approximately 6 hours to attain 90% of equilibrium (graphs 26, 28, 30 and 32). This rate is faster than the condensation resins, but is slow compared with conventional ion exchangers. The rates are however independent of metal ion and pH, as Gregor[49] observed using a m-phenylene diglycine resin with nickel (II) ions. Gregor studied the rates of

equilibration over a pH range 3 to 6 using 0.001m. metal ion solution. The resin attained maximum capacity after approximately 10 hours, this value is of the expected order for condensation resins. Degeiso[47] and co-workers using their salicylic acid-formaldehyde polymer suggested that the rates of equilibration of metal ions were independent of metal ion and its concentration. Their salicylic acid resin attained 90% equilibration in 1 hour. The idea of rate of equilibration being independent of metal ion concentration is doubtful. The XAD2 azo, oxine, alizarin and P.A.R. resins were allowed to equilibrate with 0.1m cobalt solutions at room temperature. With the oxine and P.A.R. resins 90% attainment of equilibration was reached within 30-60 minutes, the alizarin resin required slightly longer, but less than 3 hours. (Table 29). The theory of ion-exchange kinetics is well-established, evidence from literature[111] indicates that the rate determining step is the interdiffusion of the exchange counter ions either in the particle (particle diffusion mechanism) or in a film of solution surrounding the resin sphere (film-diffusion mechanism). A third criterion was reported by Hojo[112] which was referred to as diffusion exchange. If the rate determining step is diffusion through the ion exchange particle, then the extent of equilibration is dependent on the radius of the spherical particle, effective diffusion coefficient and time. If the film diffusion mechanism is the controlling factor then equilibration is governed by time and a constant, which is defined by the parameters of the film, and the diffusion coefficient of the ions through the liquid. If the rate determining step is controlled by mass action, then the extent of equilibration is dependent on time and a value S which is equal to the sum of a proportionality constant X mole fraction of say

sodium ions plus a proportionality constant x mole fraction of hydrogen ions. The majority of kinetic equilibration studies have been limited to Dowex A-1[113-116], and the variables which apparently govern these kinetics are numerous. If these variables are not closely controlled then the conclusion drawn from the results are totally misleading. This happened with Rieman and co-workers[113,114], who in their first paper suggested that exchange is controlled by a second order chemical reaction and not by diffusion. They later corrected their statement in line with other workers'[115, 116] ideas that diffusion is the rate controlling step. The particle diffusion mechanism and the appropriate equation used to determine the extent of equilibration is valid for concentrations higher than 1N and invalid if the composition of the external solution alters with time. This latter variable is true for the kinetics studied for the XAD2 resins. It has also been shown with Dowex A1 and $MgCl_2$[115] that the kinetics are independent of concentration, and that diffusion coefficients are dependent on the radius of hydrated cation, so to categorically state which process is governing the kinetics of the XAD2 resins is impossible. It is possible that the mass action effect is a major influence, which may affect the diffusion process which in turn will govern the overall kinetics.

Table 29

Period of shaking in hours	% attainment of equilibrium		
	XAD2 azo oxine	XAD2 azo P.A.R.	XAD2 azo Alizarin
½	92	85	82
1	94	90	84
2	95	93	88
4	99	94	92
7	100	98	97
24	100	100	100
48	100	100	100

Table 30

Metal Ion	Resin	Final pH variation	Temperature °C	Graph reference
Cu^{2+}	Oxine condensation acid catalysed	6.3-6.5	27	1
	Oxine condensation base catalysed	6.2-6.3	26	2
	Alizarin condensation	6.1-6.3	24	4
	Salicylic acid condensation	6.0-6.2	23	6
	Oxine azo coupled to p-azo phenol-formaldehyde copolymer	6.0-6.1	23	8
	Resin No.1	5.3-5.4	23	10
	Resin No.2	5.3-5.4	23	12
	Resin No.3	5.3-5.4	23	14
	Resin No.4	5.3-5.4	23	16
	N.R.F.	6.1-6.3	23	20
	N.R.F.P.	6.2-6.3	23	22
Cu^{2+}	XAD2 azo-oxine	5.4-5.5	27	26
U^{6+}		3.0-3.2	27	26
Cu^{2+}	XAD2 azo -	5.4-5.6	27	28
U^{6+}	P.A.R.	2.9-3.1	27	28
Cu^{2+}	XAD2 azo -	5.5-5.6	26	30
U^{6+}	Alizarin	3.0-3.1	29	30
Cu^{2+}	XAD2 azo-	5.3-5.4	29	32
U^{6+}	Salicylic acid	2.7-2.8	29	32

The uranyl capacities of the four XAD2 resins are low, which is possibly a result of the citrate buffer in competition with the resin for metal ions. When these capacities were measured using only 0.1m uranyl nitrate solutions, the values practically doubled (Table 31).

Table 31

$UO_2(NO_3)_2$ Concentration	resin capacities m.moles/g.			
	XAD2 azo -oxine	XAD2 azo- P.A.R.	XAD2 azo- Alizarin	XAD2 azo - Salicylic
0.1m	0.166	0.193	0.138	0.246
0.05m	0.077	0.114	0.074	0.226

This variation of capacity is not due to pH effects as the measurements were made at the optimum pH. It is therefore undoubtedly due to the citric acid present. If the citrate uranyl complex stability constant (average value.) is taken as 8.5^{110}, then using a simple ratio of:

$$K_{resin} = \frac{K_{complex} \times \text{total capacity when ligand present}}{\text{difference in total capacities}}$$

where $K_{complex}$ is the stability constant for uranyl citrate, and the total uranyl capacities when citrate is present are obtained from graphs 33 and 34, and when the ligand is absent from Table 31. Using this mathematical ratio, the following uranyl resinate stabilities were calculated:

XAD2 azo-oxine log K = 8.8

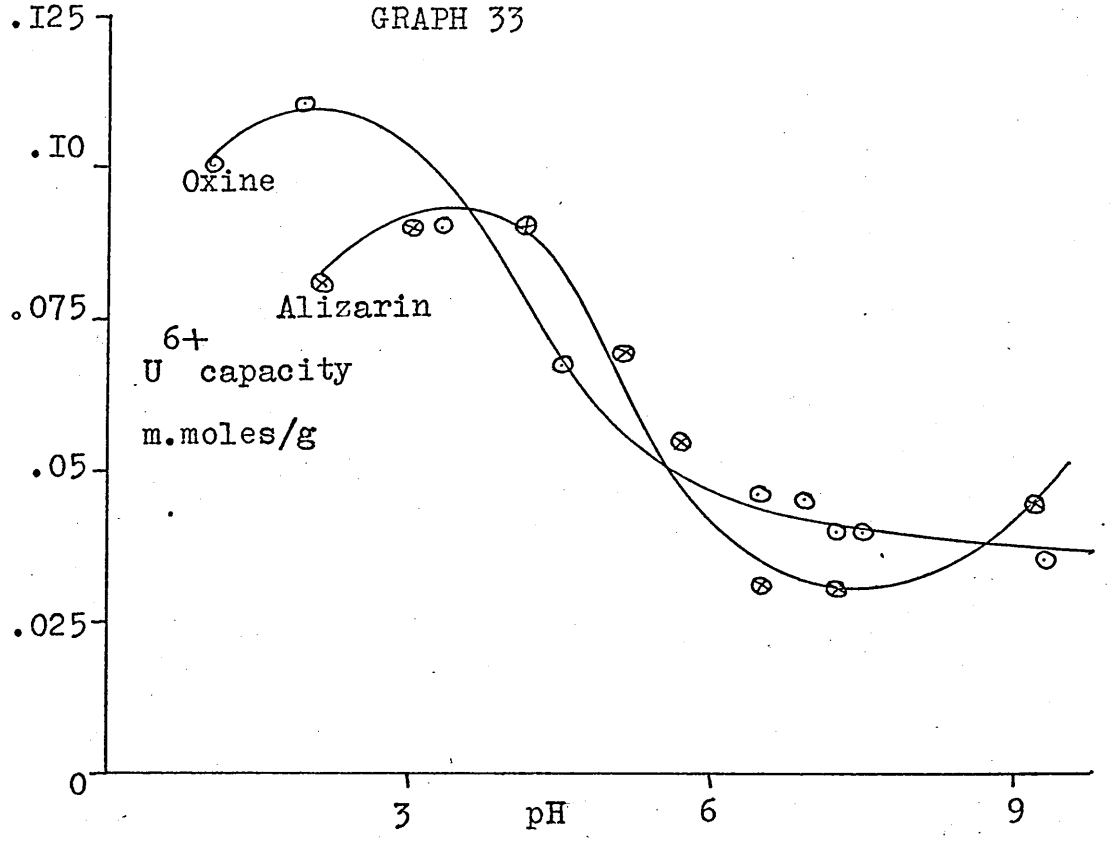
XAD2 azo-salicylic acid log K = 8.52

XAD2 azo-P.A.R. log K = 8.84

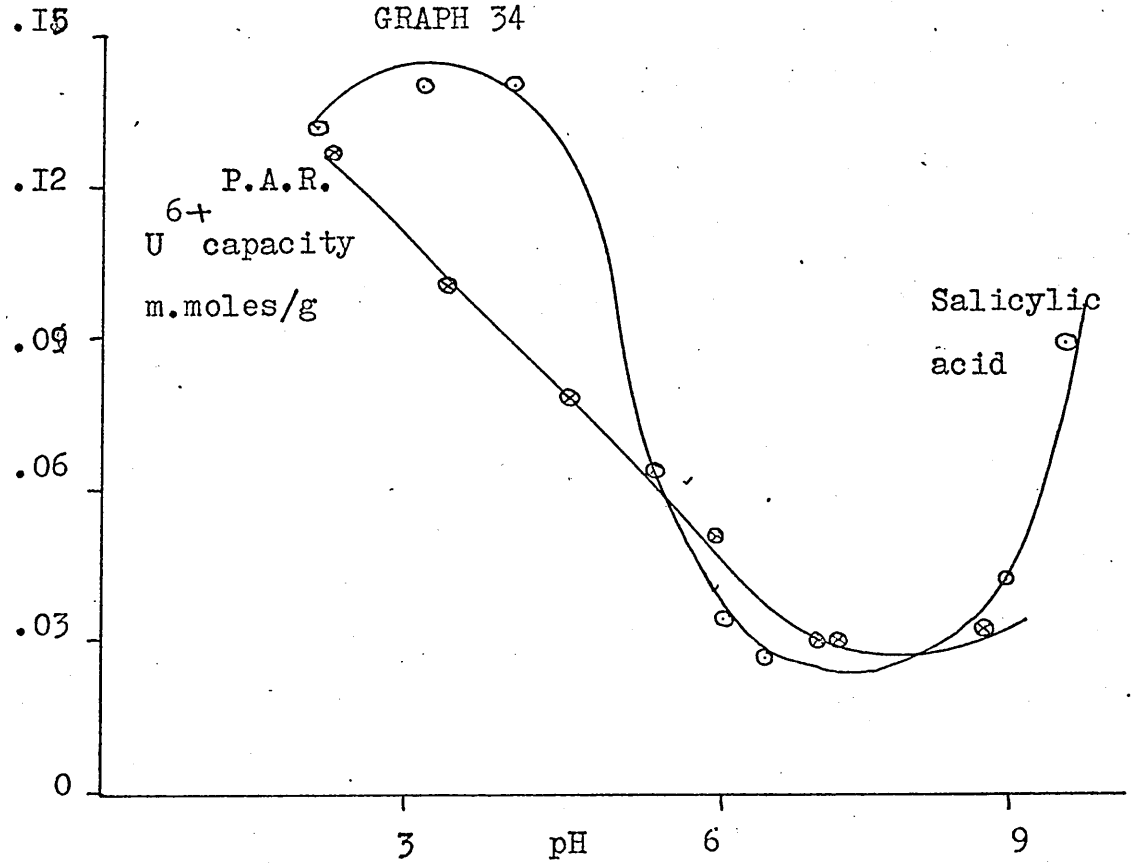
XAD2 azo-Alizarin log K = 8.76

XAD2 azo-RESINS.

GRAPH 33



GRAPH 34



This treatment gives an approximate indication only, as the concentration of citrate in solution is not considered as having an appreciable effect. The ratio of competing ligand concentration to the number of chelating sites within the resin is high, and would therefore affect the equilibrium position. A second limitation is the choice of competing ligand, with citrate the stability constant limits decided by this mathematical technique are $10^{6.8}$ (lower limit) and $10^{9.8}$ (upper limit) if the capacity for uranyl was 1 m.mole/g.

The uranyl capacities of the four resins decreased when a more dilute solution of uranyl nitrate (0.05m) was used. From the values in Table 31 it is evident that the affinity of the XAD2 azo-salicylic acid resin is stronger than the other three resins, which is contrary to the previous predictions regarding stability constants. The decrease in capacity as the uranyl concentration decreases could be due to one of two effects:-

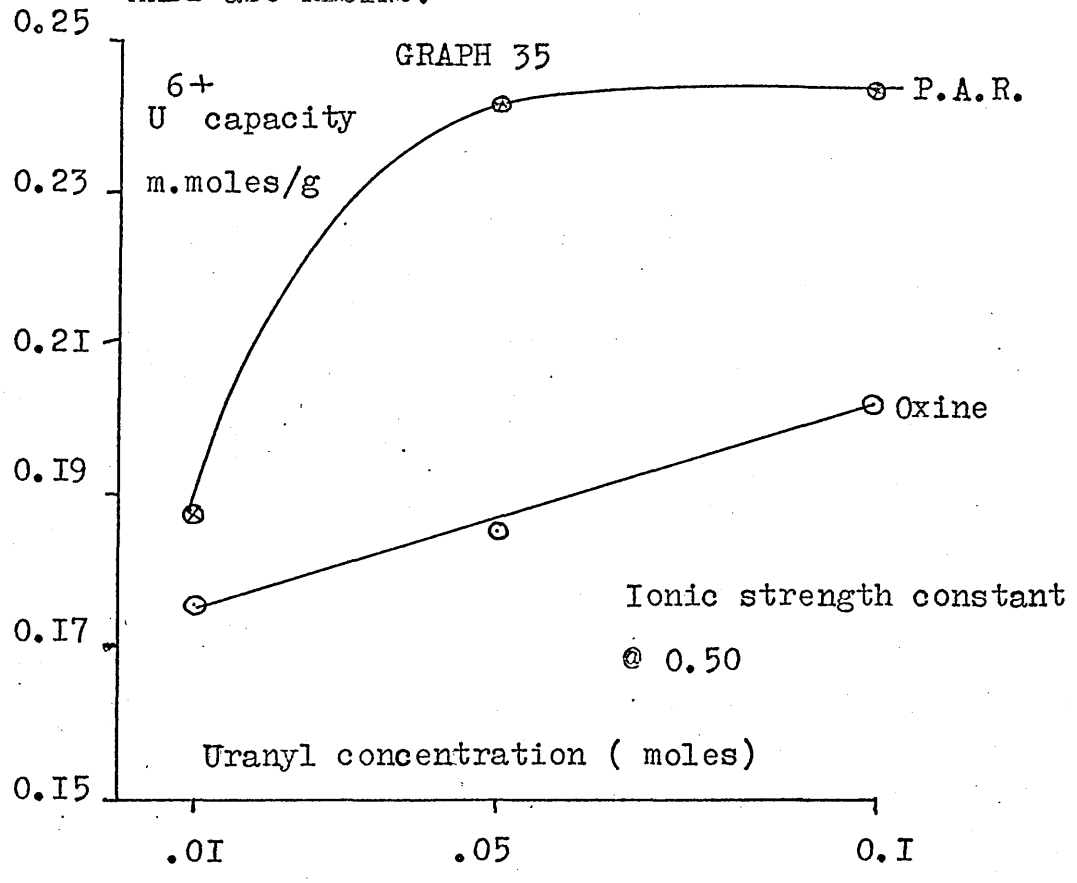
(a) decrease in uranyl ions is the predominant factor; or

(b) the ionic strength of the system is the governing step.

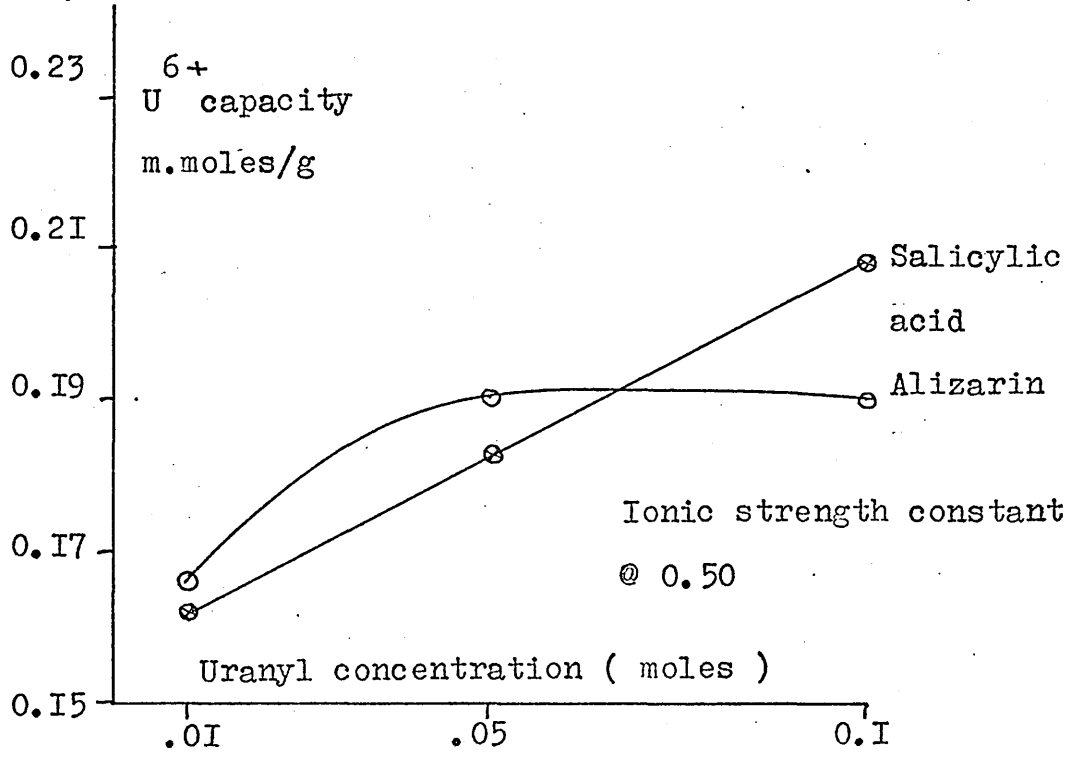
Using uranyl solutions varying from 0.01m to 0.1m (pH relatively constant between 2.8-3.1) with a constant ionic strength of 0.50 using sodium nitrate, it was found that increasing the metal ion concentration accounts for only 10-20% increase in the capacity (Graphs 35 and 36). If the capacities of the appropriate resin (Table 31) are compared with values in graphs 35 and 36 at the same metal ion concentration, then with 0.1m uranyl nitrate solutions only ($\mu = 0.3$) the capacities increase by 15-25% with the exception of XAD2 azo-salicylic acid which shows a decrease of the same magnitude. For the 0.05m uranyl nitrate solutions ($\mu = 0.15$), as ionic strength of the system increases

XAD2 azo-RESINS.

GRAPH 35



GRAPH 36



to 0.50, the capacities increase by 50-60%, again except XAD2 azo-salicylic acid. It is reasonable to assume therefore that at 0.05 to 0.1 m metal ion concentrations both ionic strength and metal ion concentration are of equivalent contribution. At low metal ion concentrations the ionic strength of the medium outweighs that of metal ion concentration. The reason for the results on the salicylic acid resin could be the dependency upon the ratio of sodium ions to uranyl ions in solution, since this resin is the only one to contain a carboxylic acid group.

Table 32

Uranyl salt	Capacity of XAD2 azo-resins			
	Oxine	P.A.R.	Alizarin	Salicylic
0.05m acetate	0.377	0.413	0.208	0.538
0.05m chloride	0.205	0.236	0.216	0.227
0.10m chloride	0.223	0.267	0.263	0.252

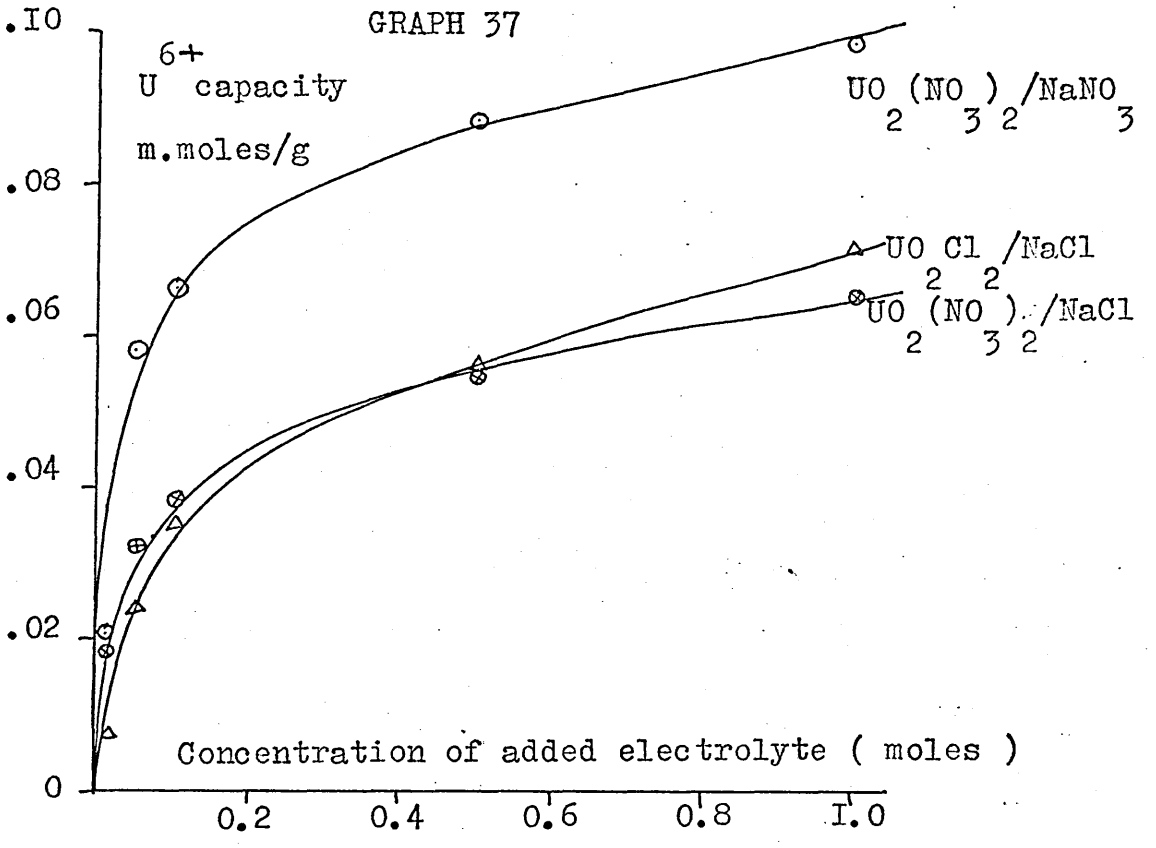
values in m.moles/g.

From table 32, it is evident that not only does ionic strength and concentration of metal ion influence the capacity at a constant pH value, but also the co-ion in solution. The reason for uranyl acetate producing capacities higher than those of chloride which in turn are higher than the nitrate, will not be based upon the relative stabilities of these species in solution. The high capacity for the uranyl acetate, can be explained in terms of the solubility of this salt in water i.e. 7.7 g./100 ml. at 15°C (0.18m). The solution used i.e. 0.05m. would be nearer it's saturation point than the nitrate or chloride. This would not be true however for

explaining why the chloride system has higher capacities, since uranyl chloride is more soluble than the nitrate. From the values in Table 32, the question arises why does uranyl concentration have little effect on capacities when chloride is present, when nitrate is present however an increase of 50% is observed? This is true for three of the resins the exception being the salicylate resin. It is possible that the salicylate group is the predominant factor in this case. If it was due to the uranyl system XAD2 azo-PAR could be expected to have an equivalent capacity for uranyl whether present as the chloride or nitrate. In an attempt to explain this, various uranyl systems were studied. These were $UO_2(NO_3)_2/NaNO_3$; $UO_2(NO_3)_2/NaCl$; $UO_2(NO_3)_2$/acetic acid; $UO_2Cl_2/NaCl$ and UO_2(acetate)$_2$/acetic acid. The results obtained are plotted as a function of the increase in capacity due to the corresponding addition of electrolyte. The capacity of the resins for uranyl ions when only uranyl nitrate solution was present was measured, say b m.moles. The capacity on the addition of electrolyte is obtained, say c m.moles. Therefore the increase in capacity due to the addition of electrolyte is (c - b) m.moles. This variable is plotted against concentration of added electrolyte. From these systems (Graphs 37-40) it appears that sodium nitrate in conjunction with the uranyl nitrate has the greatest effect on increasing the capacities. This will be due to the common ion effect, but an equivalent increase would be expected for the uranyl chloride-sodium chloride system. With the uranyl nitrate-sodium chloride system, above 0.1 m concentrations, the salt has a suppressing effect on the metal ion uptake.

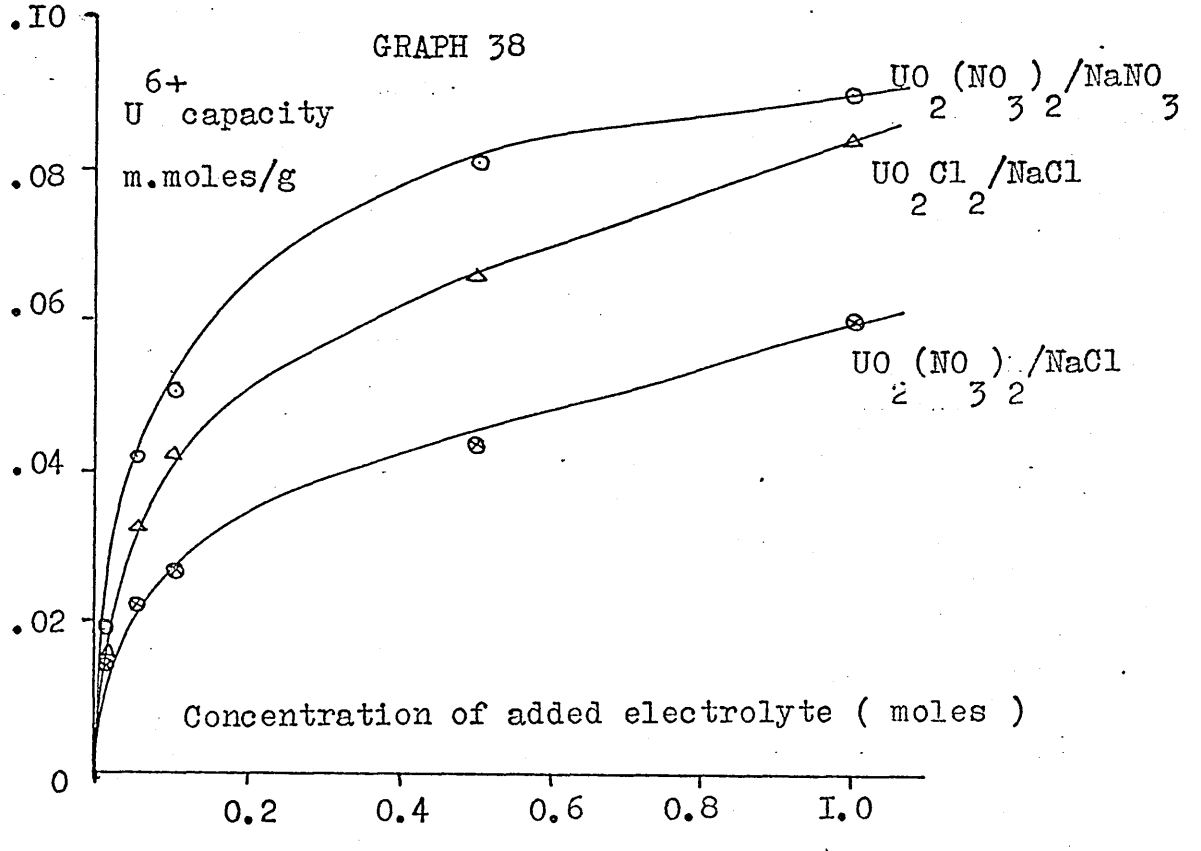
XAD2 azo-OXINE.

GRAPH 37

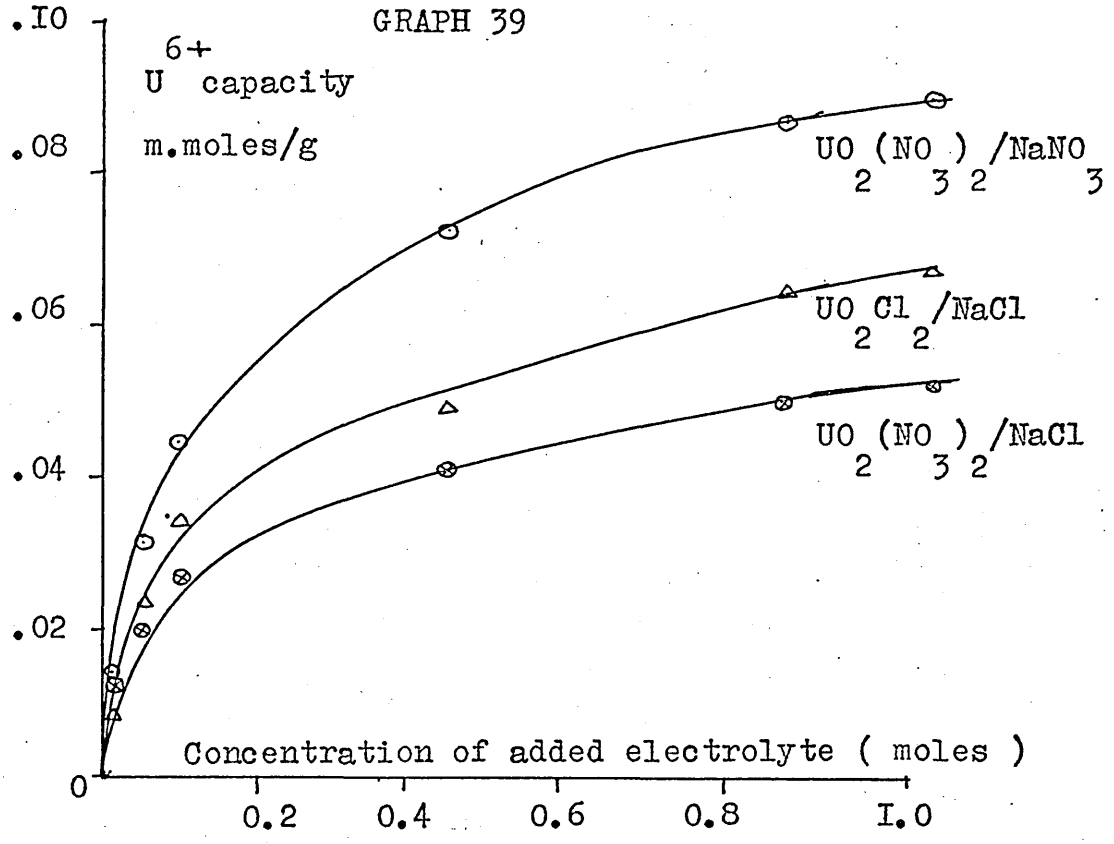


XAD2 azo-P.A.R.

GRAPH 38



XAD2 azo-ALIZARIN.



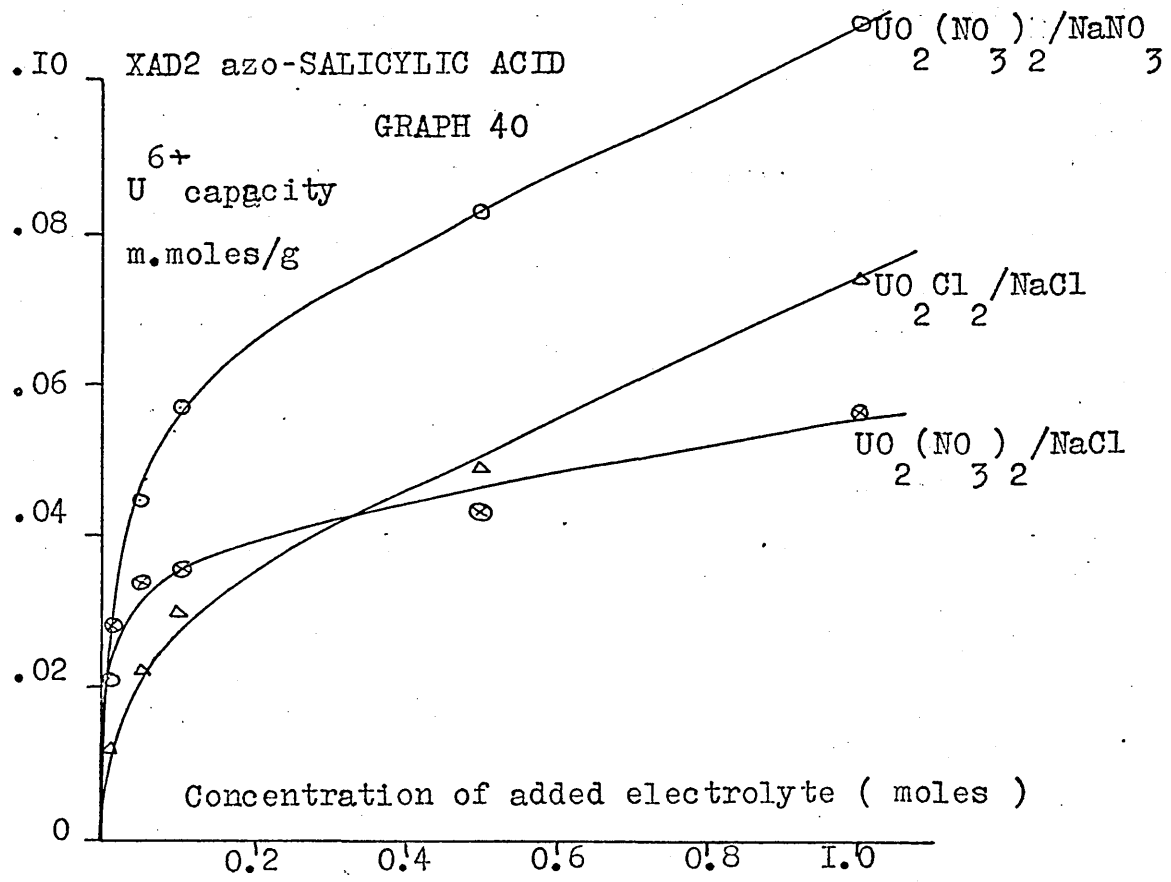


Table 33

Uranyl system	Resin capacity m.moles			
	Oxine	P.A.R.	Alizarin	Salicylic
$UO_2(NO_3)_2$	0.060	0.079	0.031	0.073
UO_2Cl_2	0.057	0.079	0.048	0.061
$UO_2(acetate)_2$	0.112	0.151	0.070	0.140

This suppression of capacity as chloride content increases could be due to the chloride ions attacking the remaining amino groups of the resin, i.e. acting as an anion exchanger. At low chloride concentrations the equilibrium is in favour of uranyl uptake. This should also be true for the uranyl chloride-sodium chloride system, but the capacities increase proportionately as chloride content increases. The difficulty in asigning the factors contributing to the capacities in these systems are numerous and variable. These variables will be dealt with individually :

(1) The possibility of the resins acting as anion exchangers due to the residual amino groups has already been discussed. This effect would tend to favour anionic complexes, such as $[UO_2Cl_4]^{2-}$, $[UO_2(NO_3)_3]^-$. From the amino contents of the resin (Table 23), XAD2 azo-salicylic acid and alizarin resins should have the highest capacities, this is only partially correct however.

(2) The reason for the uranyl acetate system having the highest capacity has been previously explained. The assumption that uranyl

formed the complexed $[UO_2(acetate)_3]^-$ molecule is likely since a small volume of acetic acid had to be added to adjust the pH to a value equivalent to that of an 0.05m $UO_2(NO_3)_2$ solution. The suggestion, from amino contents, that XAD2 azo-salicylic acid and alizarin have the highest capacities, is incorrect - alizarin has the lowest measured capacity.

(3) The XAD2 azo-salicylic acid is a cationic exchanger, i.e. it has ionisable carboxylic acid groups. This would suggest therefore slightly different behaviour to the other chelate ion exchanges which contain no such ionisable groups. It may explain the affinity of this resin for uranyl solutions within the concentration range 0.05 to 0.1m. With more dilute solutions, this effect will be less pronounced, the stabilities of the complexes formed being more prominent.

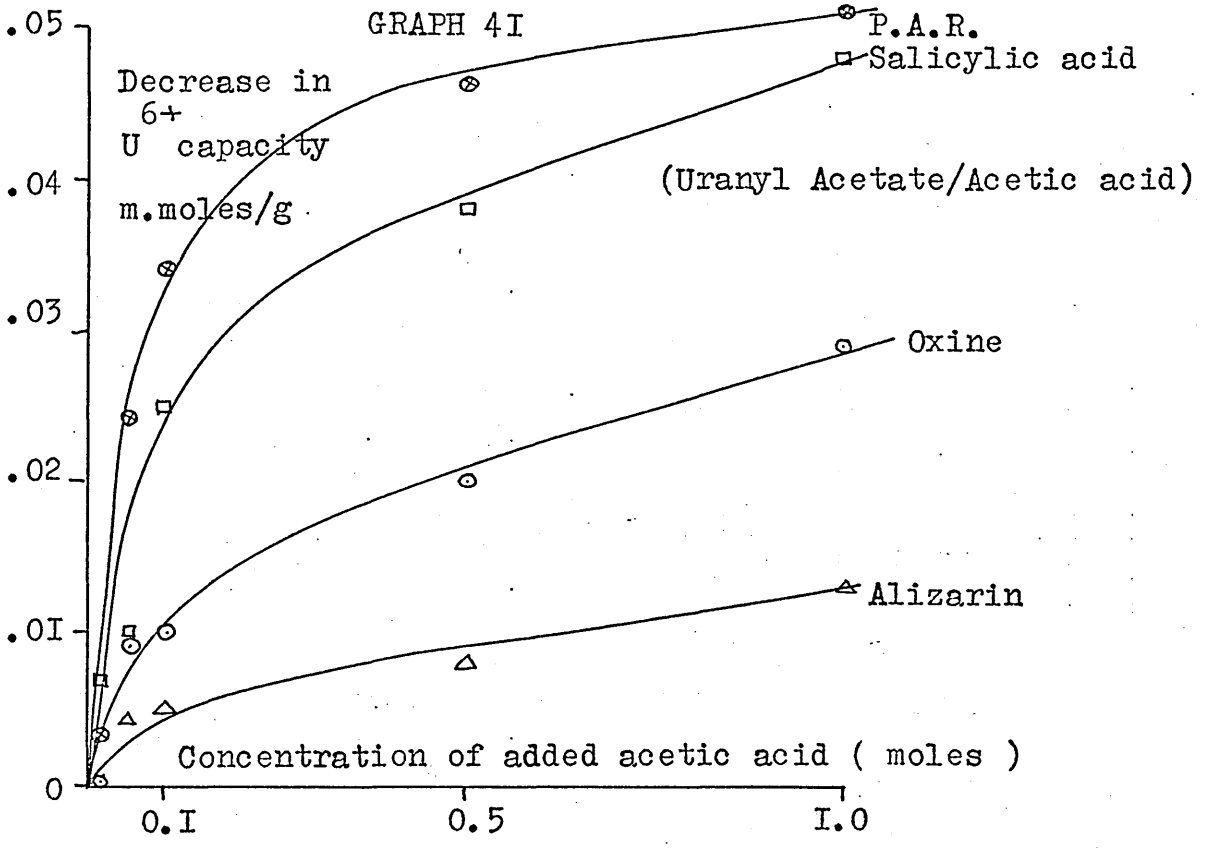
(4) All the studies with the exception of the acetic acid systems (graphs 41 and 42) indicate increasing capacities with increasing ionic strengths, this is in agreement with previous results (graphs 35 and 36).

(5) Both uranyl nitrate/acetic acid and uranyl acetate/acetic systems for all four resins show only slight deviations in the capacities when pH conditions are maintained constant at the optimum values.

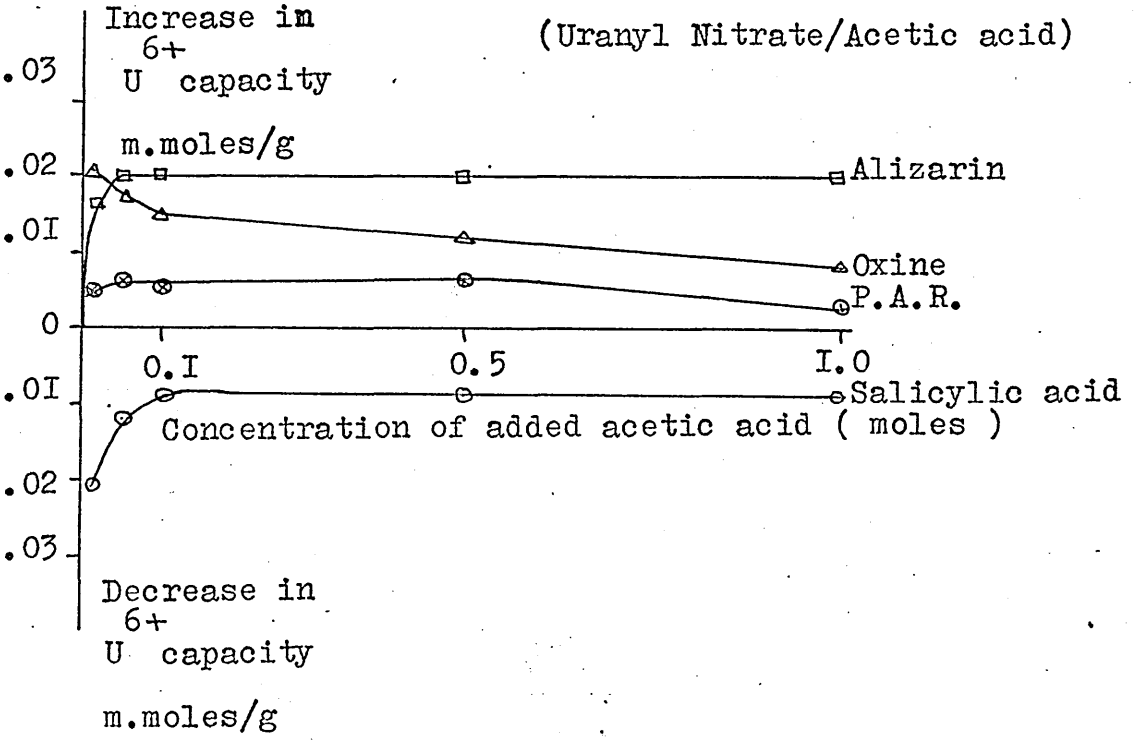
(6) To explain the behaviour of resins (except salicylic acid) towards uranyl nitrate, and uranyl chloride, it is necessary to consider both dissociation and solubility of these salts. Uranyl chloride is the more soluble salt, which produces a more

XAD2 azo-RESINS.

GRAPH 41



GRAPH 42



dissociated system. This would possibly explain the relatively high capacities for 0.1 and 0.05m uranyl chloride solutions. At lower concentrations however the dissociated molecules for both chloride and nitrate systems will tend to be equal, and the capacities as such will be equal. Uranyl acetate has the lowest dissociation value of all three uranyl systems studied, but the concentration effect will be the governing factor.

The uses of chelate ion exchangers as viable separation techniques have been limited to commercial rather than technical difficulties. The interest lies in chelate ion exchangers of the Dowex A-1 type. Dowex A-1 in particular has been extensively investigated but its applications restricted to analytical procedures. Riley and co-workers[118] used this resin for extraction of metal ions from sea water as a preliminary concentration procedure. Both inorganic absorbents and chelate ion exchangers have been reviewed as a means of uranium extraction from sea water. The difficulty appears to be at least three fold :-

(1) Uranium exists in sea water as a complexed entity $[UO_2(CO_3)_3]^{4-}$, which has a stability constant of $1.7 \pm 0.6 \times 10^{23}$, and the uranium is present in very low concentrations (3μg/ℓ).

(2) The chosen extractant must be capable of working within the pH limits of sea water i.e. 7.8 to 8.2.

(3) Possibly the most important is the selectivity of the resin or absorbent. Conventional ion-exchangers are of little value in this category, and at present few very selective chelate exchangers are known.

Using synthetic solutions of known uranyl concentration, and the four XAD2 resins, the first two stipulations were investigated. The uranyl tricarbonato complexes were prepared from uranyl nitrate-sodium carbonate, uranyl chloride-sodium carbonate, and uranyl acetate-sodium carbonate. The uranium contents of these saturated solutions were 5.89, 7.12 and 8.53 mg/ml respectively. From Table 34 the highest capacities of these resins were from the solutions containing sodium acetate. This was to be expected however as these solutions had the highest uranyl contents. The next highest should have been the solution containing sodium chloride, in fact this had the lowest capacity. This may be due to the difference in pH, or alternatively sodium chloride having an effect on the resin or uranyl complex.

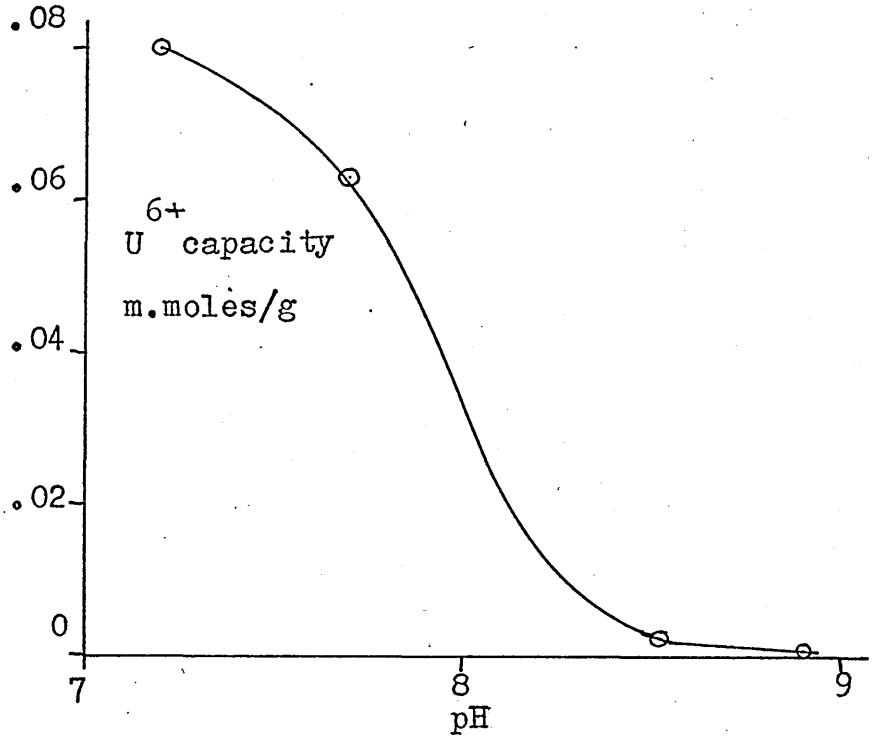
Table 34

Resin	$UO_2(CO_3)_3^{4-}$ system		pH	Capacity m.moles
	conc$^{n.}$ mg U^{6+}	medium		
Oxine	295	$NaNO_3$	7.6	0.085
P.A.R.	"	"	7.6	0.095
Salicylic Acid	"	"	7.5	0.084
Alizarin	"	"	7.6	0.100
Oxine	356	NaCl	8.5	0.037
P.A.R.	"	"	8.3	0.042
Salicylic Acid	"	"	8.1	0.044
Alizarin	"	"	8.4	0.046
Oxine	427	Na acetate	7.8	0.108
P.A.R.	"		7.6	0.115
Salicylic Acid	"	"	7.5	0.095
Alizarin	"	"	7.6	0.122

From graphs 43 and 44, it appears that the optimum pH range is 7.2 to 7.6, this lies slightly lower than the pH of sea water. The capacities at pH 7.6 are still approximately half the sodium acetate and sodium nitrate systems, which is due to the solutions used in the latter case being 20 times more concentrated. The efficiency of both these resins at the optimum pH is better than 50%. This efficiency will decrease however on approaching the pH value of sea water.

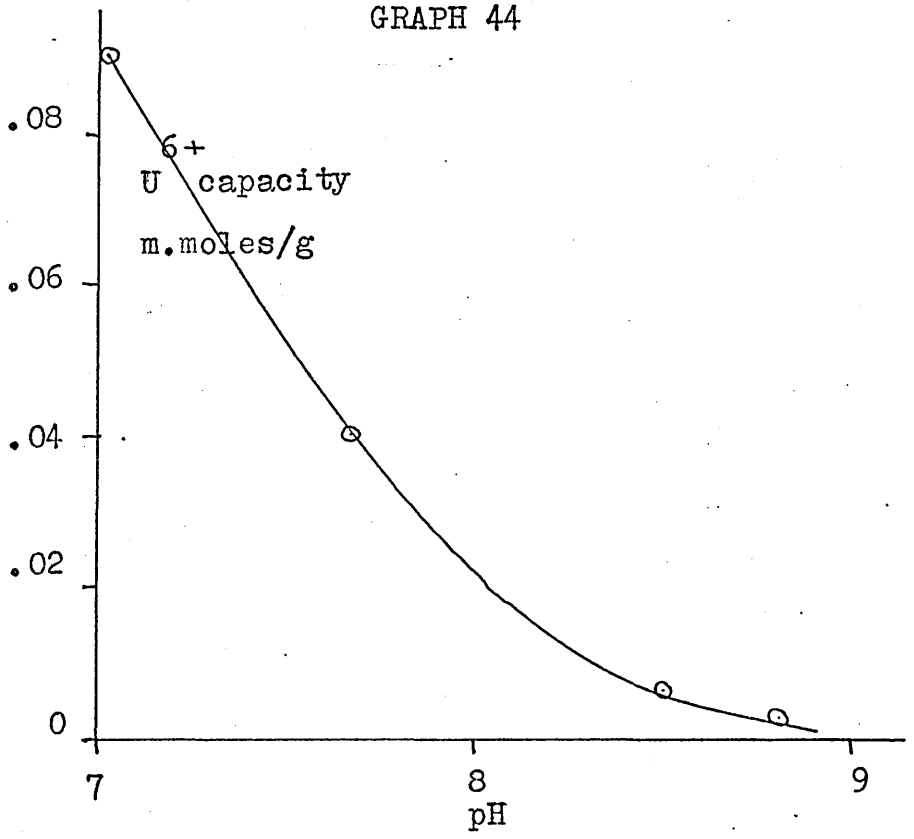
XAD2 azo-P.A.R.

GRAPH 43



XAD2 azo-SALICYLIC ACID.

GRAPH 44



DETERMINATION OF STABILITY CONSTANTS OF METAL-RESIN COMPLEXES

The determination of resin-metal ion stability constants has been restricted in the past to a few systems[25,32,76,119]. The majority of these systems studied have been with resins which were soluble in a suitable water miscible solvent, such as dioxan. The procedure adopted was the standard potentiometric titration, which generally gave fairly satisfactory results. A limited success has been achieved with the resin Dowex A-1, the stabilities of nickel and copper complexes have been studied[25], later extended by Eger et al[76] for various other metal ions, and a comparison of these values with an analogous monomeric system, N-benzyl iminodiacetic acid, made.

The difficulty with XAD2 azo-resins is that no such monomeric systems exist, and as such evaluation of these stabilities has to be attempted on the resin itself. Several procedures were attempted, and will be dealt with individually.

(1) Direct potentiometric titration

This method has been successfully used in the past, particularly by Irving and Rossotti[120] to determine the stability constants of oxine and salicylic acid complexes. For the oxine system the metal ion concentration is limited to the solubility of the metal oxinate in 50/50 water-dioxan. The procedure adopted here was to titrate the following systems using molar sodium hydroxide from a microsyringe fitted with a vernier scale.

(a) equivalent volumes of dioxan and an aqueous solution of $NaClO_4/HClO_4$.

(b) equivalent volumes of oxine (0.01m) in dioxan and an aqueous solution of $NaClO_4/HClO_4$.

(c) equivalent volumes of oxine in dioxan and an aqueous solution of copper sulphate (.005m) with $NaClO_4/HClO_4$ present.

The concentration of $NaClO_4$ was 0.600m and the $HClO_4$ 0.0385m.

From the three systems studied above it was possible to determine the stability of the copper oxinate. System (c) was repeated and 0.333g of XAD2 azo-oxine resin was added. This quantity of resin has an equivalent oxine content to that present in the aqueous phase. It should have therefore been possible to titrate this system, and hence deduce the effect the chelating ion exchanger is having on the system. Unfortunately this system was of little value, the main disadvantages with it were :

(1) low concentration of metal ions being used and hence a large proportion of the resin would have been not co-ordinated to copper (II) ions if this system had been successful.

(2) The rate of attainment of equilibrium of XAD2 azo-oxine is approximately 6 hours, therefore after each addition of alkali this system has to equilibrate. The total time required for such a titration would be of the order 3-4 days. It is possible, however, to overcome this problem by measuring the stabilities at higher temperatures, say 70-80°C, but the apparatus would have to be sealed to prevent evaporation losses.

(2) <u>"Anti-Schubert's" method</u>

Schubert's[121] method has been used on previous occasions but using conventional ion exchangers. However, the method now

connected with his name is the modified version[122] which allows for stepwise formation of a series of complexes. An ionic medium is used at constant cation concentration C_m and variations of the ligand concentration C_L are assumed not to change activity coefficients appreciably. Constant pH and trace metal concentrations are used, so that the effective ligand concentration is proportional to C_L. The resins are completely loaded with M cations. Complex formation is assumed to produce only neutral or anionic species which are supposed not to be absorbed by the resin. Keeping in mind the above restrictions, the following equation can be expressed :

$$\frac{(D^oM/DM) - 1}{C_L} = \beta_1 + \beta_2 C_L + \ldots\ldots\ldots\ldots \beta_N C_L^{N-1}$$

where D^oM is the distribution coefficient when ligand is absent and DM when ligand is present.

The "Anti-Schubert's" method is derived similarly but the competing chelate concentration (which in this case is oxine) was constant, and varying quantities of the XAD2 azo-oxine resin were employed. The results given in Table 35 indicate that this method had its limitations. The concentration and composition of the solutions were identical with those used in the potentiometric titration procedure. The initial concentration of copper ions was 7.96mg. The solutions were placed in a thermostat bath set at 25°C ± 0.1 for 1 day, after which time the resin was introduced, and equilibration allowed to proceed for 7 days with only occasional shaking at 25°C ± 0.1.

Table 35

Quantity of resin used mg	Metal ion in solution mg	Metal ion on resin mg	pH
147	7.78	0.16	2.3
183	7.65	0.31	2.3
292	7.54	0.42	2.2
79	7.92	0.04	2.2
280	6.84	1.12	2.2

The resin sample which absorbed 1.12mg of copper (II) ions, had no competing oxine molecules present in solution, only dioxan and an aqueous solution of $NaClO_4/HClO_4$ i.e.D^{o}M. The limited success of this procedure was entirely due to the final pH of the solution being of the order 2.0. As a result of this, the distribution coefficients were extremely low and possibly unreliable. This coefficient could have been increased, simply by raising the pH of the system, say to pH 5.0. This would have presumably resulted in distributions of 40-50%, which are of the desired order. However, increasing the pH of the system could have affected the solubility of the copper oxinate, similarly increasing the metal ion concentration to favour the resin capacity could have produced a precipitate or suspension of metal oxinate.

If a water soluble system was used, i.e. copper and E.D.T.A., and the solutions were sufficiently dilute so as not to contradict any assumptions made in the Schubert method, then a reasonable pH could be attained. This type of procedure was successfully employed by Loewenschuss et al[25], who determined

the stability constants for copper and nickel on Dowex A-1. The assumption made was that a fairly large chelate molecule must be employed, so that it is only the hydrated metal ion which is capable of entering the resin pores and not the metal complex. The procedure itself was that varying ratios of metal, chelate and resin were allowed to attain equilibrium at a constant pH value (for Dowex A-1 Ca. 10.0). The pH is certainly critical for XAD2 azo-resins in the region 4.5 to 5.5, as the proportional increase in capacity is greater than pH variations. The quantity of resin used was always greater than the metal ion in solution, usually a 5% allowance was made. This quantity of resin was derived from the experimental capacities previously measured in acetate medium. The final pH's of the solutions after equilibration with the resin were measured, and the samples which were of the incorrect pH were adjusted to that value with either sodium hydroxide or dilute perchloric acid. This procedure was repeated until all the samples had the same pH value. The copper concentration of the solution was measured using E.D.T.A. and P.A.N. indicator, and the known values incorporated into the following equation :

$$\frac{K_{MR}}{K_{MY}} = \frac{[MR][Y]}{[MY][R]} = K_{over\text{-}all} \qquad \text{---------- (1)}$$

where :

K MR is the stability constant of the resin-metal complex;

K MY is the stability constant of the copper-ligand complex;

[MR] concentration of metal ion in resin phase;

[Y] concentration of uncomplexed ligand left in solution.

[MY] concentration of metal complex found in solution.

[R] concentration of uncomplexed resin left.

$K_{over\text{-}all}$ is the stability constant ratio of the metal, resin and

ligand system.

This equation is derived from the following systems. When a chelating ion exchanger is allowed to equilibrate with a solution containing a metal and a large polydentate ligand, two competing complexation reactions occur.

$$M + Y \rightleftharpoons MY \qquad K_{MY} = \frac{[MY]}{[M][Y]} \qquad \text{---------- A}$$

$$M + R \rightleftharpoons MR \qquad K_{MR} = \frac{[MR]}{[M][R]} \qquad \text{---------- B}$$

Rearranging equation (1) gives

$$\log [R] = \log \frac{[MR][Y]}{[MY]} - \log K_{over\text{-}all} \qquad \text{---------- (2)}$$

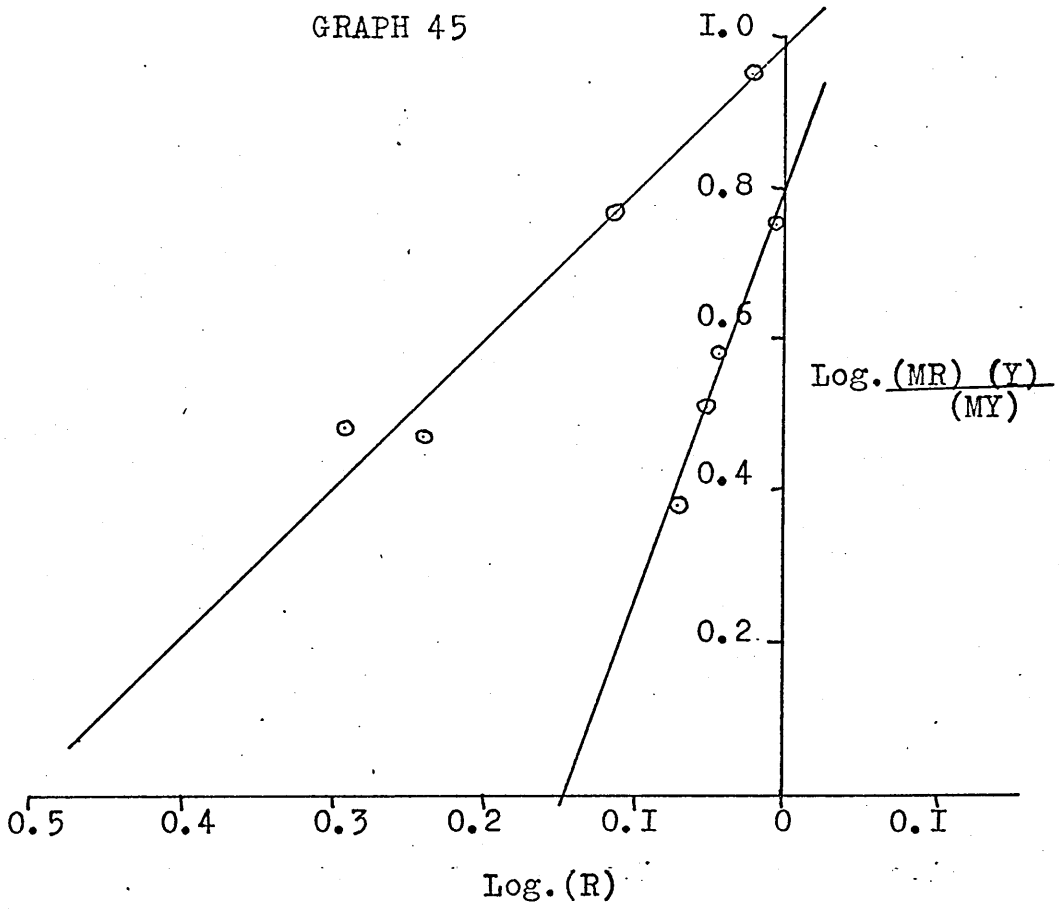
The competing ligand chosen for XAD2 azo-resins was glycine, and the metal ion was copper. The results and measurement conditions are given in Tables 36-39, and the appropriate values plotted in graphical form (graphs 45-47).

Table 36 XAD2 azo-P.A.R. resin

Concentration of Cu(II)	Concentration of glycine	Quantity of resin used. g.	[CuR]	[Y]	[MY]	[R]
1.0	2.0	3.0	0.84	1.68	0.16	0.96
"	"	2.0	0.69	1.38	0.31	0.51
"	"	2.5	0.65	1.30	0.35	0.85
1.5	3.0	3.5	1.08	2.16	0.42	1.02
"	"	4.0	1.10	2.20	0.40	1.30
"	"	2.5	0.92	1.84	0.58	0.58
"	3.5	3.0	0.95	2.40	0.55	0.85
"	3.5	2.5	0.88	2.25	0.62	0.88

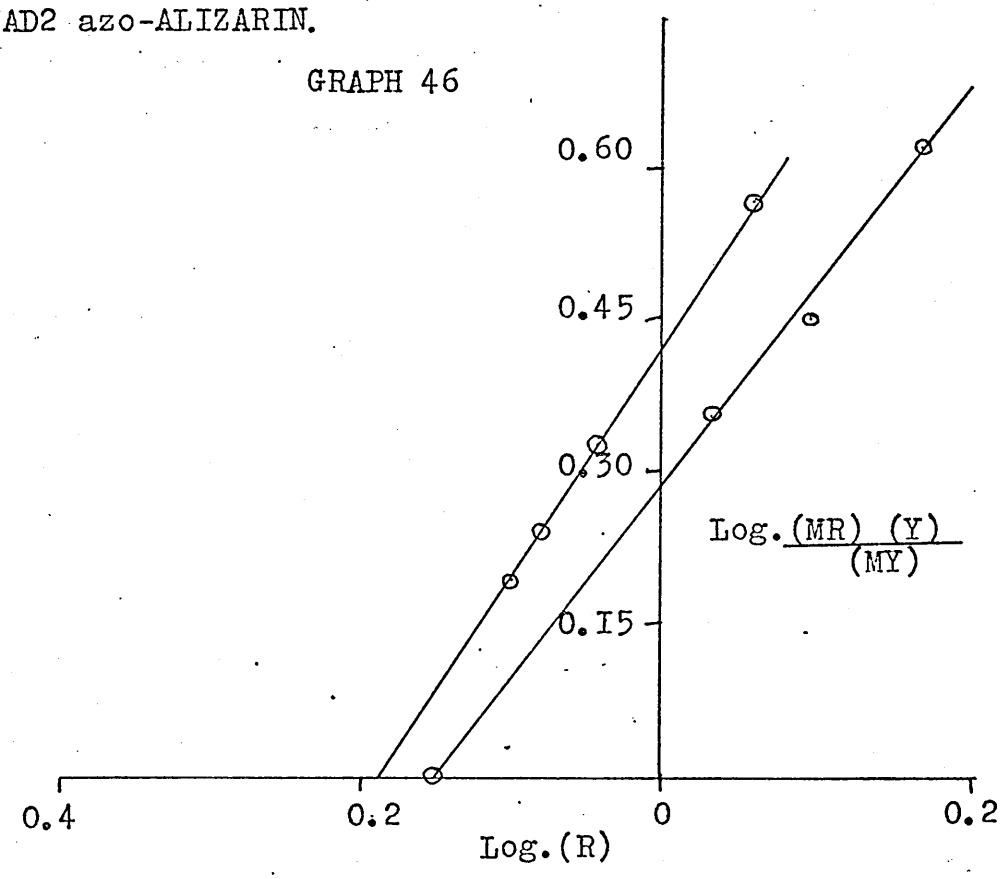
XAD2 azo-P.A.R.

GRAPH 45



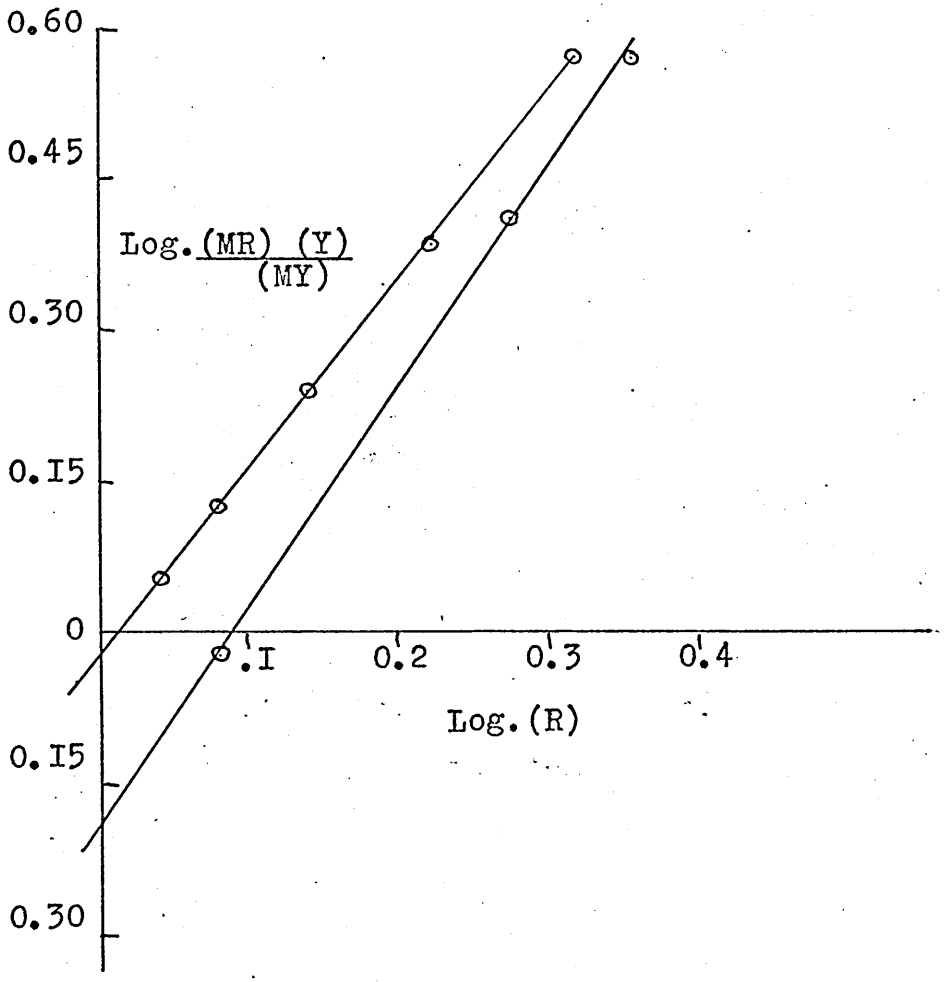
XAD2 azo-ALIZARIN.

GRAPH 46



XAD2 azo-SALICYLIC ACID.

GRAPH 47



Final pH's constant at 5.2, capacity previously measured was 0.60m. moles/g. at this pH.

Table 37 XAD2 azo-alizarin

Concentration of Cu(II)	Concentration of glycine	Quantity of resin used. g.	[CuR]	[Y]	[MY]	[R]
1.0	2.0	2.0	0.50	1.00	0.50	0.74
"	"	2.5	0.63	1.26	0.37	0.92
"	"	3.0	0.72	1.44	0.28	1.14
1.5	3.0	2.5	0.76	1.52	0.74	0.79
"	"	3.5	0.91	1.82	0.59	1.26
"	"	4.0	1.01	2.02	0.49	1.47
"	3.5	2.5	0.71	1.92	0.79	0.84
"	"	3.0	0.79	2.08	0.71	1.07

Final pH's constant at 5.2, capacity previously measured was 0.62m.moles/g. at this pH.

Table 38 XAD2 azo-salicylic acid

Concentration of Cu(II)	Concentration of glycine	Quantity of resin used. g.	[CuR]	[Y]	[MY]	[R]
1.0	2.0	1.75	0.52	1.04	0.48	1.10
"	"	2.5	0.65	1.30	0.35	1.65
"	"	3.0	0.72	1.44	0.28	2.04
1.5	3.0	2.0	0.64	1.28	0.86	1.20
"	"	3.0	0.89	1.78	0.61	1.87
"	"	3.5	0.98	1.95	0.52	2.24
"	3.5	2.0	0.65	1.80	0.85	1.19
"	"	2.25	0.71	1.92	0.79	1.36

Final pH's constant at 5.2, capacity previously measured was 0.93m.moles/g at this pH.

All the values in Tables 36-38 are expressed in m.moles except columns 3.

From equation (2) the intercept on the log $\frac{[MR][Y]}{[MY]}$ axis should give the over-all stability constant of the system. However, with all three graphs two definite straight lines were obtained. The intercepts of these are :-

XAD2 azo-P.A.R. log $K_{over-all}$ = 0.99 and 0.78.

XAD2 azo-alizarin log $K_{over-all}$ = 0.42 and 0.29.

XAD2 azo-salicylic acid log $K_{over-all}$ = -0.02 and -0.19.

The relationship for log $K_{over-all}$ is :-

$$\log K_{over-all} = \frac{\log^K MR}{\log^K MY}$$

using the overall stability constant for copper glycinate, which is 13.1, the copper resinate values were calculated (as given in Table 39).

Table 39

system	log K_1 metal -monomer (Literature value)	log K_1 metal resinate
UO_2-oxine	11.25(ref 110)	8.8
UO_2-salicylic acid	2.20-12.1 (ref 110) (Depending on complex species)	8.5
UO_2-P.A.R.	12.5 (ref 86)	8.8
UO_2-alizarin	-	8.8
Cu-P.A.R.	14.8(ref 86)	Ca 14.0
Cu-alizarin	-	Ca 13.5
Cu-salicylic acid	10.60 (ref 110)	Ca 13.0

The values obtained using the "Anti-Schubert's" method are of the same order as the stability constants of the corresponding metal-monomer complexes. These values are contrary to the uranyl constants, as the latter are lower than the corresponding metal-monomer complexes. These lower values could be due to the assumption that competing ligand concentration has little or no effect. With the "Anti-Schubert's" method, however, the competing ligand concentration is considered as a governing factor, and the results obtained by this procedure should be of some significant value. Even with this procedure however it is impossible to quote a precise metal-resinate stability constant, as some inexplicable discrepancies occurred, for instance :-

(1) two definite straight lines obtained;

(2) the gradients of these lines should be unity from the proposed mechanism (equations A and B), in fact the observed values range from 1 to 6, with the majority of values being approximately two.

It must also be emphasised that two molecules of glycine in solution chelate 1 molecule of copper (II) ion, whereas with the resin a 1:1 complex is assumed to be formed, with possibly the co-ion (nitrate) maintaining electron neutrality. These stability values are apparent constants and not thermodynamic constants, because the activity coefficients of the metals in solution and in the resin phase have been neglected.

(3) Stary's Method

The procedure adopted by Stary[17] was to examine a series of metal oxinates by solvent extraction, when several competing water soluble ligands were present. From these results he was able to calculate the stability constants of the metal chelate knowing the stability constants of the metal oxinates. A slight modification was employed using the XAD2 azo-oxine, and P.A.R. resins, in place of oxine and solvent extraction. The equilibration time for this system was somewhat longer than Stary's procedure, in this case two days were allowed. The metal ion chosen was copper and the competing ligands were oxalic acid, tartaric acid, E.D.T.A. and 1, 2-diaminocyclohexane tetra-acetic acid (C.D.T.A.). With this procedure the pH was varied over the required range, to obtain these pH's either perchloric acid (N/10) or sodium hydroxide (N) were used.

Procedure - to a solution containing a known quantity of copper nitrate (which was 0.1M with respect to sodium perchlorate) an equivalent volume of water was added. A small quantity of either sodium hydroxide or perchloric acid, was added depending on the required pH. This quantity of acid or alkali was known from a previous potentiometric titration of an identical system. The solutions were shaken for two minutes and 0.250g of the appropriate resin added. The systems were allowed to attain equilibrium for two days with occasional shaking. The pH was measured and the final copper concentration of the solution determined. This procedure was repeated using the four competing ligands. The quantity of ion (copper) on the resin was expressed as a % extraction, as the initial metal

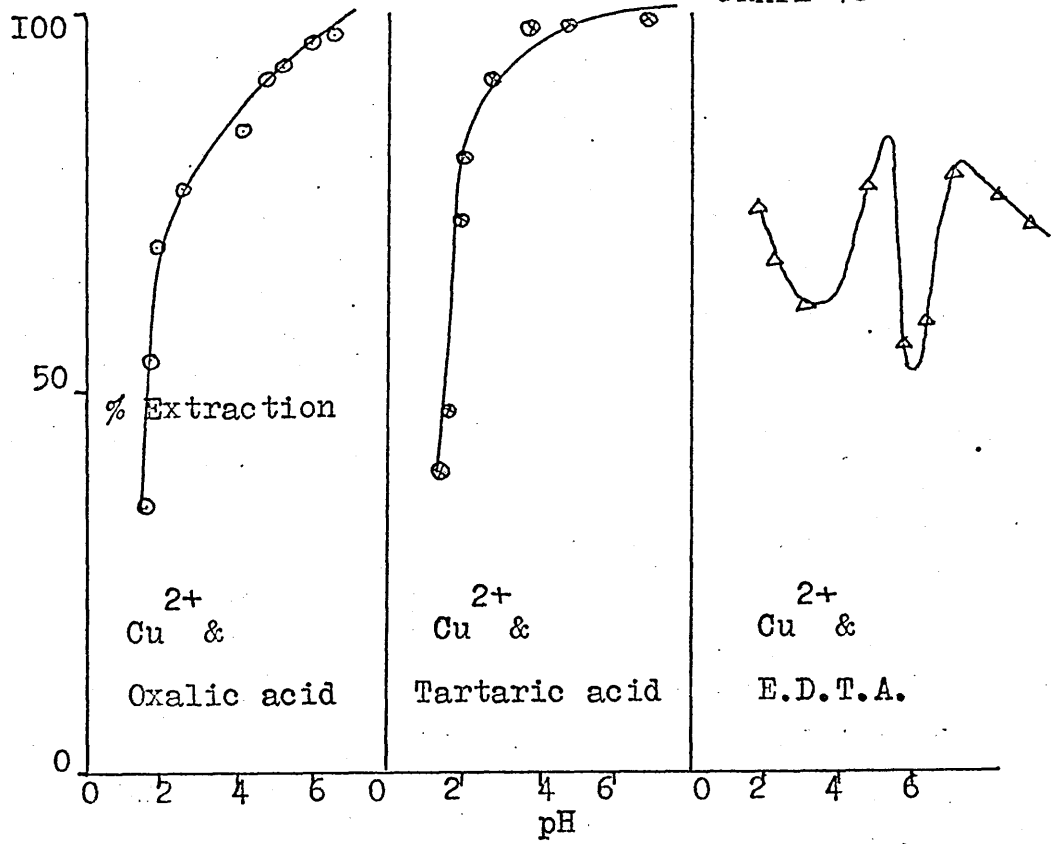
ion concentration was known. The results are expressed in graphical form (graphs 48-50). The quantity of resin chosen was sufficient to absorb all the metal ion from solution. From the graphical data the behaviour of the oxine resin was analogous to oxine monomer when used in solvent extraction procedures, with the exception of C.D.T.A. With this ligand the % extraction was zero over a pH range of 2.8 to 9.3, indicating that the stability of the copper-C.D.T.A. complex was greater by a factor of at least 100 than copper-resin complex. Unfortunately only a qualitative idea of the metal-resinate stability constant can be predicted. The calculations employed by Stary required the pH at 50% extraction. It is evident from the graphs 48-50 that there is very little difference in the pH at which 40 and 70% extractions are obtained.

From the procedures previously discussed, the possibility of determining a precise value for a metal-resin stability constant appears to be highly unlikely. The numerous difficulties with these methods appear to limit the concept of metal-resin stability to a qualitative idea. Of the methods investigated the most promising technique appears to be the Anti-Schubert's method employing water soluble complexes. The criterion appears to be choosing a suitable competing ligand and having a homogeneous resin with only one functional group.

The chelating abilities of the Resin 2 (azo-oxine resin derived from 4-Nitroso-Resorcinolpolymer) and the p-phenol azo - oxine resin were investigated using copper and nickel glycinates. The results are given in Table 40.

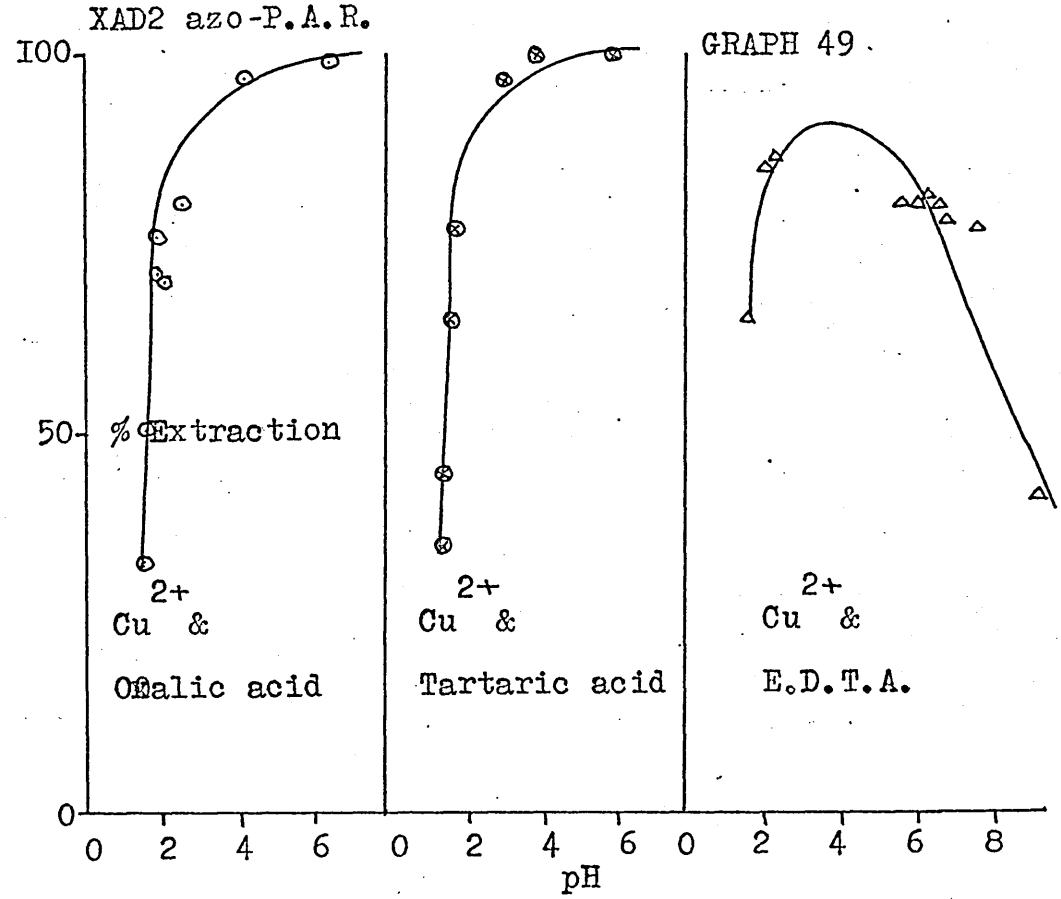
XAD2 azo-OXINE.

GRAPH 48



XAD2 azo-P.A.R.

GRAPH 49



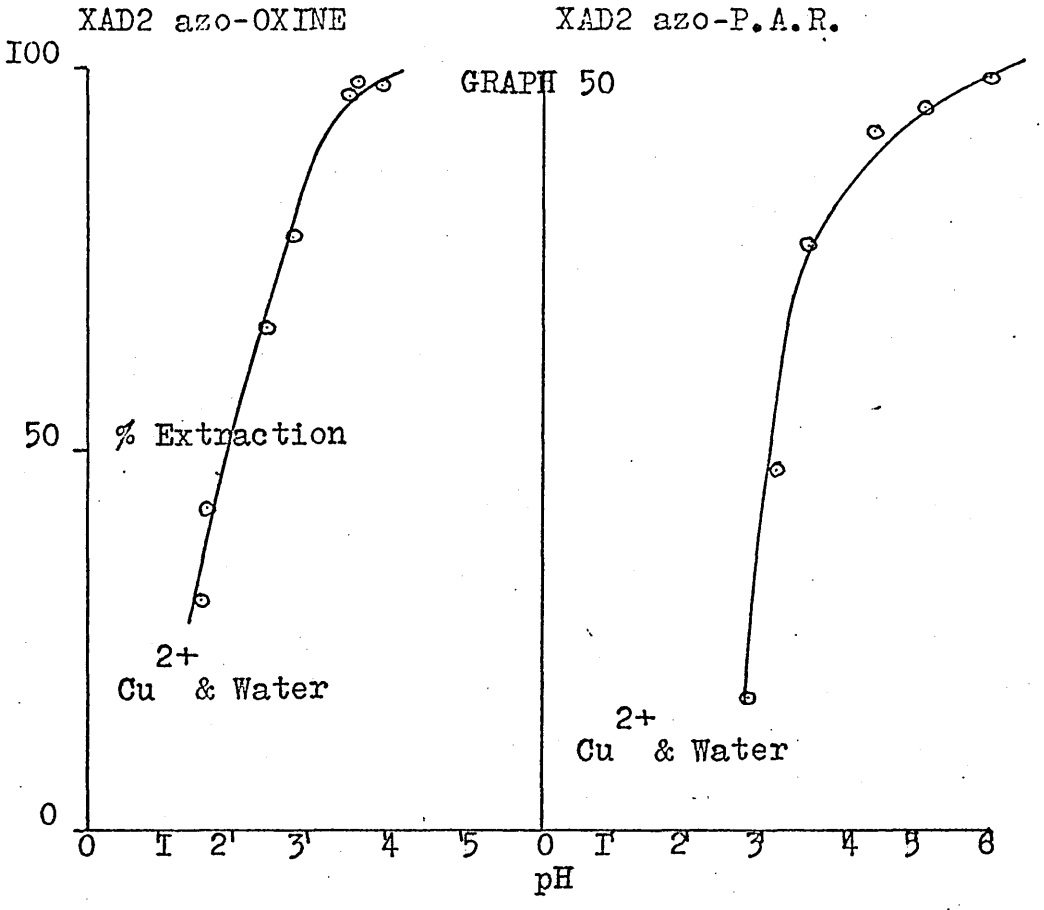

XAD2 azo-OXINE
XAD2 azo-P.A.R.
GRAPH 50
100
50
0
% Extraction
2+
Cu & Water
2+
Cu & Water
0 1 2 3 4 5 0 1 2 3 4 5 6
pH

Table 40

Resin	Metal ion	Measured capacities m.moles		% decrease due to glycine
		0.2m glycine	Acetate buffer	
Resin 2	Co^{2+}	0.06	0.88	93
	Ni^{2+}	0.04	0.63	94
p-azo-phenol oxine	Co^{2+}	0.22	0.50	56
	Ni^{2+}	0.16	0.28	43

From these values it can be concluded that the metal ion complex formed with the p-azo-phenol oxine resin is much more stable than the corresponding complex formed with Resin 2. It is possible therefore that during the investigation of Resins 1, 2 3 and 4 all the oxine units were chelated initially and the remaining capacity obtained by chelation of metal ions to the nitroso groups or possibly the azo linkages. This treatment is only qualitative, since the glycine in equilibrium with the resin was of greater concentration than the chelating groups within the resin.

A second qualitative technique employed during this investigation was to allow resins to equilibrate with a particular metal ion at a definite pH value. The loaded resin was then allowed to equilibrate with a second metal ion at the same pH and the distribution of exchange measured. The systems chosen were XAD2 azo-oxine and Resin 1 (azo-oxine resin derived from a 4-Nitroso-Resorinol polymer), cobalt ions (0.1m), uranyl ions (0.1m) and a pH

value of 8.6. Unfortunately with this pH value a complexing agent was necessary and 0.2m tartaric acid was used. To observe the effect this competing ligand was having on the capacities, cobalt capacities of both resins at pH 8.6 were measured with tartaric acid present. Similarly the uranyl capacity was also measured at this pH value. The values obtained are given in Table 41.

It was assumed that a metal ion having a higher stability constant with the resin, would displace other metal ions of lower stability. This is a feasible idea, but the difficulty found with this technique was the difference in the structure of the complexes formed between uranyl ions and the resin and cobalt ions and the resin.

Table 41

Resin	Co(II) capacity m.moles/g.	U(VI) capacity m.moles/g.	Co(II) capacity after equilibrating with uranyl solution m.moles/g.	U(VI) capacity m.moles/g.
XAD2 azo-oxine	0.33	0.09	0.27	0.03
Resin 1	1.63	0.08	1.00	0.08

From the tabulated results one third of the available sites were occupied by uranyl ions for the XAD2 azo-oxine resin, whereas with Resin 1 all the sites were occupied. The difficulty with the latter resin was that the remaining nitroso groups formed a stronger complex with cobalt (II) than with uranyl ions, or possibly the uranyl ions will not form a complex

at all. This technique seems to be a more interesting qualitative approach to metal ion stabilities, the difficulty being choosing two suitable metal solutions requiring no complexing agent and a resin with one functional group.

The oxine chelate ion exchangers prepared by direct condensation techniques proved to be unsatisfactory in that the capacities were very low and the rates of equilibration were also low. This is contrary to the resins prepared by Pennington and Williams and Degeiso, but verifies work by Parrish. The difficulty with direct condensation resins is that mode of chelation and structure cannot be easily demonstrated. Certainly the acid catalysed resin had a different structure, than the one prepared by Degeiso et al. The alizarin and salicylic acid condensation resins were more successful, but also had limitations. The alizarin resin was unstable, which resulted in the chelating groups being leached out of the resin matrix. This in turn produced low capacities and the rate of equilibration was poor. Although the salicylic acid resin initially appeared to be successful from the sodium-hydrogen exchange value, the difficulties later encountered were that the resin matrix was too dense to allow the larger hydrated metal ions to enter, thus producing rather low capacities and rate of equilibration.

The oxine exchangers prepared by azo coupling of this molecule to suitable condensation resins produced exchangers of higher capacities, but relatively the same kinetics. The capacities of the resins in general could be equated to metal-oxinate stabilities, but owing to the intervention of other functional groups only a qualitative idea can be obtained. The difficulty with resins prepared by azo coupling of oxine molecules to a matrix derived from 4-Nitroso-Resorcinol, was the low conversion of nitroso groups to amino, thus resulting

in the final resin having two functional groups. One of the two nitroso exchangers had metal ion capacities superior to most other chelate exchangers previously reported, but the kinetics were again too slow.

The coupling of chelate molecules to a diazonium styrene-divinyl benzene copolymer, produced superior exchangers. Although these resins were not selective for the metal ions studied, the rates of equilibration were of practical viability. The capacities for the metal ions examined were complicated however by other "chelating" sites within the resin phase. These values were comparable with the metal-ligand monomer stability constants. The presence of these other "chelating" sites caused difficulties when investigating uranyl absorption. The possibility that these resins could behave as ordinary anion exchangers (due to amino groups) when allowed to equilibrate with uranyl systems at low pH values i.e. 1.5-2.5 could not be ignored.

The determination of metal-resin stabilities achieved limited success but did furnish sufficient information to warrant a more detailed studied using uni-functional resins.

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